ELSEVIER

Journal of Molecular Catalysis A: Chemical 157 (2000) 41–58

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Synthesis and catalytic activity of allyl, methallyl and methyl complexes of nickel(II) and palladium(II) with biphosphine monoxide ligands: oligomerization of ethylene and copolymerization of ethylene and carbon monoxide

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Received 13 August 1999; accepted 8 December 1999

Abstract

The syntheses of new cationic nickel complexes {[η^3-methallyl]Ni[κ^2P,O-$Ph_2P(X)P(O)Ph_2$]}SbF_6, (**1**)–(**2**) [X = (*o*-C_6H_4) (**1**), (NH), (**2**)] have been accomplished. The complexes oligomerize ethylene to linear α-olefins with selectivities as high as 89%. A dependence of oligomerization grade and activity on backbone geometry was shown. New cationic allyl and methyl complexes of palladium(II) [$(CH_3CN)(Me)Pd(\kappa^2P,O–Ar_2P(CH_2)_nP(O)Ar_2)]X$ [$n = 1–3$, $X = BF_4$, $Ar = C_6H_5$ (**18**–**20**)] [$n = 1$, $X = SbF_6$, Ar = *p*-tolyl (**23**); $n = 1$ or 2, $X = SbF_6$, $Ar = C_6H_5$ (**21**) or (**22**)]; [(η^3-C_3H_5)$Pd(\kappa^2P,O$-$Ph_2P(CH_2)_nP(O)Ph_2)]X$, [$n = 2$, X = triflate (**10**), tosylate (**13**); $n = 3$, X = triflate (**11**), tosylate (**14**)], [(η^3-C_3H_5)]$Pd(\kappa^2P,O$-$Ar_2P(CH_2)_nP(O)Ar_2)]X$, [$n = 1$, $X = SbF_6$, Ar = *p*-tolyl (**17**); $n = 2$, $X = SbF_6$ $Ar = C_6H_5$(**16**)] have been synthesized in good yields. These complexes have been used in the catalytic oligomerization of ethylene, and in the catalytic alternating copolymerization of ethylene and carbon monoxide, to yield polyketones. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Biphosphine monoxide; Nickel; Palladium; Ethylene oligomerization; Polyketones; Ethylene/CO cooligomerization

Abbreviations: cod, 1,5-cyclooctadiene; dppacet, *o*-diphenylphosphino acetophenone; dppanis, *o*-diphenylphosphino anisole; dppaO, bis(diphenylphosphino)amine-monoxide; $dppaO_2$, bis(diphenylphosphino)amine-dioxide; dppbald, *o*-diphenylphosphino benzaldehyde; dppbenzaMe, *o*-diphenylphosphino benzoic acid methylester; dppeO, 1,2-bis(diphenylphosphino)ethane-monoxide; dppmO, bis(diphenylphosphino)methane-monoxide; dppOPh, (*o*-diphenylphosphino)phenyl-phenylether; dpppaEt, 3-diphenylphosphino propionic acid ethylester; dppbenzO, 1,2bis(diphenylphosphino)benzene-monoxide; dpppO, 1,3bis(diphenylphosphino)propane-monoxide; dppres, 2,5-(dimethoxy)phenyl-diphenylphosphine; dtolpmO, bis(di *o*-tolylphosphino)methane-monoxide; eq., equivalent

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PII: S1381-1169(99)00449-5

1. Introduction

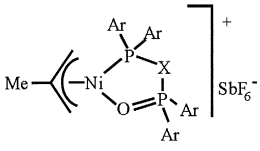
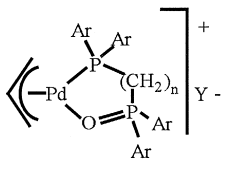
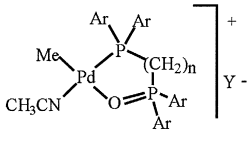
It is widely known that organo-nickel and -palladium complexes containing phosphine ligands exhibit outstanding catalytic activity in a large number of organic reactions, e.g., carbon–carbon linkage reactions [1,2].

A great interest focuses on the synthesis and catalytic application of transition metal complexes with chelating ligands containing phosphorus and oxygen donor atoms (in the following: P ^O, [3]; for a review, see Ref. [4]).

One of the most important applications of transition metal compounds for industry is their use as catalysts in oligomerization and polymerization of olefins [5,6]. Among the used metals are the early transition metals, e.g., zirconium and titanium, as well as the late transition metals like nickel and palladium [7–9].

Neutral and cationic nickel complexes with chelating ligands, e.g., P ^O, N ^N, N ^N ^N, O ^O, have been successfully applied in the oligomerization of olefins [10–14]. Among those ligands, anionic P ^O-ligands play an important

Table 1
Numbering of the methallyl nickel(II), allyl palladium(II) and methyl palladium(II) cationic complexes used (*: new complexes; see Ref. [30] and references therein for other complexes)

	X= *o*-C_6H_4 dppbenzO (**1**)*	X= NH dppaO (**2**)*	X= CH_2 dppmO (**3**)	X= $(CH_2)_2$ dppeO (**4**)	X= $(CH_2)_3$ dpppO (**5**)
	Y= BF_4	n= 1 dppmO (**6**)	n= 2 dppeO (**7**)	n= 3 dpppO (**8**)	
	Y= CF_3SO_3	n= 1 dppmO (**9**)	n= 2 dppeO (**10**)*	n= 3 dpppO (**11**)*	
	Y= *o*-$TolSO_3$	n= 1 dppmO (**12**)	n= 2 dppeO (**13**)*	n= 3 dpppO (**14**)*	
	Y= SbF_6	n= 1 dppmO (**15**)	n= 2 dppeO (**16**)*	n= 1 dtolpmO(**17**)*	
	Y= BF_4	n= 1 dppmO (**18**)*	n= 2 dppeO (**19**)*	n= 3 dpppO (**20**)*	
	Y= SbF_6	n= 1 dppmO (**21**)*	n= 2 dppeO (**22**)*	n= 1 dtolpmO (**23**)*	

role and are applied in the oligomerization of ethylene (SHOP-process Shell) [15].

The use of cationic nickel complexes with neutral P ^O-ligands has only been scarcely reported in literature [16].

Matt et al. [17] synthesized a cationic nickel complex from a neutral SHOP-like precursor by protonation of the neutral complex, but no data for catalytic activity of the cationic complex is given. Ecke [18] and Schulz [19] reported on the application of cationic (P ^O-chelated) nickel complexes and their catalytic activity in the oligomerization of olefins. A comparison between catalytic results of neutral and analogous cationic complexes showed that the latter exhibits a dramatic increase in activity but has a lower selectivity to linear and higher α-olefins. This behaviour was ascribed to a loss of chelate coordination of the P ^Oligand under catalytic conditions.

A polymerization reaction that has recently risen to industrial application is the alternating copolymerization of ethylene and carbon monoxide to alternating polyketones [20]. Polyketone itself is a very interesting polymer because of its properties [21] and because of the ease of functional group interconversion [22]. Recent studies have dealt with the mechanistic explanation of the stereoregularity of this copolymer, investigating ligand-induced stereocontrol and chain end control [23,24].

It has also been reported [25] how cooligomers of ethylene and CO may selectively be obtained using cationic palladium(II) complexes with P ^O and P ^S ligands. The effect of hemilabile ligands in catalysis with nickel(II) and palladium(II) complexes, and the possible mechanistic activation pathways, have been elucidated by several studies [26–28]. Polymerization, catalyzed by palladium(II) methyl complexes with P ^O, N ^O, and tridentate P ^N ^O ligands, has also been described [29].

We previously have reported on the synthesis and characterization of cationic nickel(II) and palladium(II) complexes with the monoxides of diphosphine ligands dppm, dppe, and dppp [30]. For palladium, it was shown that the coordination mode of the ligand is dependent on the backbone and on the anion, revealing a monodentate coordination, when stronger coordinating anions, such as triflate or tosylate, were used.

We now want to report on the catalytic activity exhibited by these complexes (Table 1) towards ethylene oligomerization and ethylene/CO alternating copolymerization and on the synthesis of some additional new complexes.

2. Experimental

2.1. Materials and apparatus

All syntheses and catalysis runs were carried out using standard Schlenk techniques under argon as inert gas. All solvents were dried and distilled under argon. Ethylene (Gerling and Holz 99.5%) and CO (Linde 99.99%) were used as received; $AgSbF_6$ and $KPPh_2$ (0.5 M in THF) were purchased from Aldrich; $AgCF_3SO_3$ and Ag(*p*-tolSO_3) were purchased from Fluka; $AgBF_4$ and Celite™ were purchased from Fluka.

The ligands dppmO, dtolpmO [31], and dppaO [32], were prepared according to literature methods; dppeO, dppbenzO, and dpppO [33] were synthesized in a modified way according to the patent literature given. The complexes bis[(η^3-methallyl)nickel(II)bromide] [34], {(η^3-methallyl)(η^4-1,5-cyclooctadiene)nickel(II)}hexafluoroantimonate [35], bis[(η^3-allyl)palladium(II)iodide] [36], and [(chloro)(methyl)(η^4-1,5-cyclooctadiene)palladium(II)] [37], were synthesized according to the literature.

Gas-chromatograms were obtained on Siemens Synchromat systems equipped with a 25-m SE 54-CS column using nitrogen as carrier gas, or with a 100-m Pona CB using helium as carrier gas. Yields of ethylene oligomers were obtained with the use of the internal standard method (nonane). The molecular weights

of the alternating copolymers were determined by GPC using HFIPA as eluent. A typical GPC probe contained 10 mg of polymer dissolved in 2 ml solvent.

NMR spectra in solution were recorded on a Bruker DPX 300 or a Bruker AM-300 instrument; ^{13}C MAS CP NMR spectra were recorded on a Bruker AM-300 Spectrometer. The numbering of the allyl/methallyl ligand in NMR data is as follows: H^1(syn) H^2(anti)-C^1C^2(H^5 for allyl, Me for the CH_3 group of methallyl) C^3H^4(syn)H^3(anti). C^1 is *trans* to P.

^{31}P NMR chemical shifts relative to 85% phosphoric acid are reported with positive values downfield from the reference. IR spectra were recorded on a Nicolet 510 P FT spectrometer. The samples were prepared as a Nujol mull and placed between KBr plates or as CH_2Cl_2 solutions between KBr plates. Secondary ion mass spectrograms (SIMS) were obtained on a Finnigan MAT 95 spectrometer with the following matrixes: 3-nitrobenzylalcohol (NBA); a mixture of 1,4-dithio-DL-threitol; 1,4-dithioerythritol; sulfolane (DTT/DTE/Sul) or a 10:1 mixture of 18-crown-6/tetraethyleneglycoldimethylether (K/T). Elemental analyses were performed on a Carlo Erba 1106 CHN analyser.

2.2. Complex synthesis

2.2.1. Synthesis of complexes (η^3-methallyl)[P^P(O)-κ^2-P,O]nickel(II) anion **1**–**2**

To a suspension of about 0.5 mmol [(η^3-methallyl)NiBr]$_2$ in 10 ml dichloromethane at −20°C, a solution of 2.0 eq. of the biphosphine monoxide in 5 ml of the same solvent is added while stirring vigorously. The resulting red-brown suspension is stirred for 30 min. Silver bromide, precipitating after the addition of a solution of $AgSbF_6$ in 5 ml of dichloromethane, is filtered off through Celite™ after a maximum reaction time of 5 min. The clear yellow filtrate is collected at −20°C. The solvent is removed in vacuo, yielding a yellow powder that is washed with diethylether and *n*-pentane. After drying in vacuo, the complexes are obtained in analytically pure form. Scales and yields are given in Table 2. Analytical data for the new complexes are given in Section 2.3. All data for other complexes have been previously reported [30].

2.2.2. Syntheses of complexes (η^3-allyl)[bis-(diarylphosphino)alkane-monoxide-κ^1-P/κ^2-P,O]palladium(II) anion (**10**), (**11**), (**13**), (**14**), (**16**), (**17**)

To a solution of {(η^3-allyl)[bis(diarylphosphino)alkane-monoxide-κ^1-P](iodo) palladium (II)} in a 5 ml of dichloromethane, 1.0 eq. of silver salt in dichloromethane is added at room temperature. Precipitation of silver iodide occurs immediately, and the mixture is stirred for a maximum reaction time of 5 min. It is then filtered through Celite™ and the clear, colourless, or pale yellow filtrate solution is evaporated to about 2 ml. By adding 15 ml of *n*-pentane, an off-white or pale-yellow solid precipitates. The complexes **10**, **11**, **13**, **14**, **16** and **17** can be obtained as powders in analytically pure form after the decanting from the solvent and the drying in vacuo. Scales and yields are given in Table 3. Analytical data for the new complexes are given in Section 2.3. All of the data

Table 2
Scales and yields for the preparation of complexes **1** and **2**

Number	Ligand	mg and mmol	[(η^3-C_4H_7)NiBr]$_2$	$AgSbF_6$	Yield
1	dppbenzO	716 mg	294 mg	522 mg	1.12 g
		1.55 mmol	0.76 mmol	1.52 mmol	1.38 mmol (91 %)
2	dppaO/dppaO_2 (mixture)	536 mg	235 mg	417 mg	0.80 g
		1.34 mmol	0.606 mmol	1.21 mmol	1.06 mmol (88%)

Table 3
Scales and yields for the preparation of complexes **10**, **11**, **13**, **14**[a]

Complex	Ligand	mg and mmol	$[(\eta^3\text{-}C_3H_5)PdI]_2$	AgX	Yield
10	dppeO	396 mg	261.1 mg	244.7 mg (triflate)	604.3 mg
		0.956 mmol	0.476 mmol	0.952 mmol	0.85 mmol (89%)
11	dpppO	343 mg	219 mg	206 mg (triflate)	510 mg
		0.8 mmol	0.4 mmol	0.8 mmol	0.7 mmol (88%)
13	dppeO	380 mg	251 mg	260 mg (tosylate)	520 mg
		0.917 mmol	0.457 mmol	0.932 mmol	0.709 mmol (78%)
14	dpppO	342 mg	219 mg	223 mg (tosylate)	500 mg
		0.8 mmol	0.4 mmol	0.8 mmol	0.67 mmol (84%)

[a]Complexes **16** and **17** were prepared according to literature methods [30]; these complexes show the same analytical data for the organometallic cation with respect to their analogues bearing BF_4^- as the counteranion.

for other complexes have been previously reported [30].

*2.2.3. Synthesis of complexes [(Me)Pd(P ^P(O))(CH_3CN)] anion (**18**), (**19**), (**20**), (**21**), (**22**), (**23**)*

To a solution of [(Cl)(Me)Pd(P ^P(O)-κ^2-P,O)] or $[(Cl)(Me)Pd(P\ \hat{}\ P(O)\text{-}\kappa^1\text{-}P)]_2$ in 5 ml of dichloromethane and 1 ml of acetonitrile (excess), 1.0 eq. of silver salt in dichloromethane or dichloromethane/acetonitrile is added at room temperature. Precipitation of silver chloride occurs immediately, and the mixture is stirred for a maximum reaction time of 5 min. The mixture is filtered through Celite™, and the clear, colourless, or pale-yellow filtrate solution is evaporated to about 2 ml. By adding 15 ml of *n*-pentane, a white solid precipitates. Complexes **18**–**23** can be obtained as powders in analytically pure form after the decanting from the solvent and the drying in vacuo. Scales and yields are given in Table 4. Analytical data for the new complexes are given in Section 2.3.

2.3. Spectroscopic properties

*2.3.1. {(η^3-Methallyl)[1,2-bis(diphenylphosphino)benzene-monoxide-κ^2-P,O]nickel(II)}hexafluoroantimonate, [(η^3-methallyl)Ni(dppbenzO)]SbF_6 (**1**)*

Anal. Calc. for $C_{34}H_{31}F_6NiOP_2Sb$ (812.04): C, 50.29; H, 3.86. Found: C, 49.91; H, 4.19. ^{1}H

Table 4
Scales and yields for the preparation of complexes **18**–**23**

Complex	Ligand	(P ^PO)Pd(CH_3)Cl or $[\{(\mu\text{-}Cl)(Me)Pd(P\ \hat{}\ P(O)\text{-}\kappa^1P)\}_2]$	AgX	Yield
18	dppmO	736 mg	263 mg	770 mg
		1.32 mmol	1.35 mmol X = BF_4	1.19 mmol (90%)
19	dppeO	137 mg	48 mg	147 mg
		0.24 mmol	0.25 mmol X = BF_4	0.22 mmol (92%)
20[a]	dpppO	156 mg	51.6 mg	147 mg
		0.26 mmol	0.26 mmol X = BF_4	0.22 mmol (85%)
21	dppmO	796 mg[b]	440.5 mg	770.1 mg
		1.24 mmol	1.28 mmol X = SbF_6	0.96 mmol (77%)
22	dppeO	194.9 mg	118.4 mg	247.7 mg
		0.341 mmol	0.345 mmol X = SbF_6	0.305 mmol (89%)
23	dtolpmO	394.2 mg	226.0 mg	519.3 mg
		0.643 mmol	0.658 mmol X = SbF_6	0.608 mmol (94%)

[a]In the presence of excess acetonitrile (0.15 ml).
[b]Complex: (dppmO)Pd(CH_3)Cl · CH_2Cl_2 (crystalline).

NMR (CD_2Cl_2, 300 MHz, 293 K): [ppm] δ = 1.68 (s, 1H, H^1), 1.99 (s, 1H, H^2), 2.19 (s, 3H, Me), 3.60 (s br, 1H, H^3), 4.34 (s br, 1H, H^4), 7.00–8.50 (m, 24H, Ar).). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz, 293 K): [ppm] δ = 23.3 (s, Me), 49.4 (d, J = 3.8 Hz, C^3), 77.8 (d, J = 18.5 Hz, C^1), 127.4–136.6 ($C^2 + C_{arom}$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121 MHz, 293 K): [ppm] δ = 16.4 (d, J = 28.1 Hz, PPh_2), 47.3 (d, J = 28.1 Hz, $P(O)Ph_2$); IR (Nujol): [cm^{-1}] ν = 1461 vs, 1377 vs, 1306 w, 1146 w, 1120 m, 1083 w, 1051 w, 1027 w, 738 m, 723 m, 656 s, 546 m. SIMS (NBA), cation: m/z [$I_{rel.}$(%)] = 575 (100) [(methallyl)Ni(dppbenzO)]$^+$, 520 (19) [Ni(dppbenzO)]$^+$, 401 (4), 385 (24), 281 (5), 73 (89); anion: m/z ($I_{rel.}$/%) = 235 (100) $[SbF_6]^-$.

2.3.2. (η^3-Methallyl)[bis(diphenylphosphino)-amine-monoxide-κ^2-P,O]nickel(II)hexafluoroantimonate, [(η^3-methallyl)Ni(dppaO)]SbF_6 (2)

Anal. Calc. for $C_{28}H_{28}F_6NNiOP_2Sb$ (750.9): C, 44.78; H, 3.77; N, 1.87. Found: C, 44.76; H, 3.92; N, 1.89. ^1H NMR (CD_2Cl_2, 300 MHz, 293 K): [ppm] δ = 2.17 (s, 3H, Me), 5.74 (br s, 1H, NH) 6.50–8.50 (m, 20H, Ar) (the resonances of allylic protons are broadened at 293 K due to fluctuation). ^1H NMR (CD_2Cl_2, 300 MHz, 267 K): [ppm] δ = 1.80 (s, 1H, H^1), 2.17 (s, 3H, Me), 2.67 (br s, 1H, H^2), 3.41 (m, 1H, H^3), 4.41 (s, 1H, H^4), 5.74 (br s, 1H, NH), 6.50–8.50 (m, 20H, Ar). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz, 293 K): [ppm] δ = 22.3 (s, Me), 126.2–133.6 (C_{arom}) (the resonances of allylic carbon atoms are broadened at 293 K due to fluctuation). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121 MHz, 293 K): [ppm] δ = 65.7 (d, J = 27.0 Hz, PPh_2), 71.5 (d, J = 27.0 Hz, $P(O)Ph_2$). IR (Nujol): [cm^{-1}] ν = 1463 vs, 1439 m, 1377 s, 1258 m, 1130 s, 1104 m, 1077 m, 1067 m, 899 vs, 734 m, 693 m, 658 vs, 532 s. SIMS (NBA), cation: m/z [$I_{rel.}$(%)] = 514 (31) [(methally)Ni(dppaO)]$^+$, 460 (12) [HNi(dppaO)]$^+$, 281 (5), 221 (4), 207 (9), 147 (18), 90 (10), 73 (100); anion: m/z [$I_{rel.}$(%)] = 235 (100) $[SbF_6]^-$.

2.3.3. (η^3-Allyl)[1,2-bis(diphenylphosphino)-ethane-monoxide-κ^2-P,O]palladium(II) trifluoromethanesulfonate [(η^3-allyl)Pd(dppeO)]-CF_3SO_3 (10)

Anal. Calc. for $C_{30}H_{29}F_3O_4P_2PdS$ (710.98): C, 50.68; H, 4.11. Found: C, 50.74; H, 4.24. ^1H NMR: (CD_2Cl_2, 300 MHz, 293 K): [ppm] δ = 2.30–2.45 (vbr, 2H, $H^{3,4}$), 2.69–2.89 (br d, J = 10.5 Hz, 4H, CH_2CH_2), 4.12 (dd, J = 9.3 Hz, J = 13.8 Hz, 1H, H^2), 5.08 (t, $J_{H,H} = J_{H,P}$ = 6.9 Hz, 1H, H^1), 5.85 (m, 1H, H^5), 7.48–7.87 (m, 20H, H_{arom}). $^{31}P\{^1H\}$ NMR: (CD_2Cl_2, 121 MHz, 293 K): [ppm] δ = 20.7 (d, J = 11.7 Hz, PPh_2), 47.9 (d, J = 11.7 Hz, $P(O)Ph_2$). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 282 MHz, 293 K): [ppm] δ = −79.19 (s). SIMS (DTT/DTE/Sul), cation: m/z [$I_{rel.}$(%)] = 561 (28) [(all)Pd(dppeO)]$^+$, 520 (2) [Pd(dppeO)]$^+$, 447 (29) [(dppeO) + SH]$^+$, 443 (7) [Pd(dppeO)–Ph]$^+$, 415 (19) [(dppeO) + H]$^+$, 368 (3), 337 (10), 291 (4) [Ph_2PPd]$^+$, 229 (25) [$Ph_2P(O)CH_2CH_2$]$^+$, 213 (14) [$Ph_2PCH_2CH_2$]$^+$, 201 (4) [Ph_2PO]$^+$, 185 (4) [Ph_2P]$^+$, 133 (100); anion: m/z [$I_{rel.}$(%)] = 149 (100) $[CF_3SO_3]^-$.

2.3.4. (η^3-Allyl)[(1,3-bis(diphenylphosphino)-propane-monoxide-$\kappa^{1,2}$-P,O)palladium(II) trifluoromethanesulfonate [(η^3-allyl)Pd(dpppO)]-CF_3SO_3 (11)

Anal. Calc. for $C_{31}H_{31}F_3O_4P_2PdS$: C, 51.36; H, 4.31. Found: C, 50.30; H: 4.30. ^1H NMR (CD_2Cl_2, 300 MHz): most abundant isomer (κ^2 P,O coordination), [ppm] δ = 1.97–1.50 (m, 2H, CH_2), 3.19–2.53 (m, 6H, $Ph_2(P{=}O)CH_2$, CH_2PPh_2, H^4, H^3),[1] 3.67 (dd, 1H, H^2), 4.50 (t, 1H, H^1), 5.75–5.64 (m, 1H, H^5), 7.83–7.00 (m, 20H, H_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): (most abundant isomer, κ^2 P,O coordination) [ppm] δ = 13.5 (CH_2), 27.6–25.2 (m, $-Ph_2(P{=}O)CH_2$, CH_2PPh_2), 52.2 (C^3), 81.0 (d, ^2J (C,P) = 31 Hz, C^1), 119.1 (s, C^2), 132.3–126.3 (C_{arom}). ^{31}P NMR ($CDCl_3$, 121 MHz): (a) most

[1] The chemical shift of the allylic protons H^4, H^3 was determined with the aid of H,H-COSY (in $CDCl_3$) as: δ = 3.1 ppm (H^4), δ = 2.9 ppm (H^3).

abundant isomer (κ^2 P,O coordination): [ppm] $\delta = 16.5$ ($-PPh_2$), 51.2 ($-Ph_2P{=}O$), (b) less abundant isomer (κ^1 P coordination): [ppm] $\delta = 17.7$ ($-PPh_2$), 35.0 ($-Ph_2P{=}O$). ^{19}F ($CDCl_3$, 282 MHz): [ppm] $\delta = -78.5$ ($CF_3SO_3^-$). IR (nujol mull): $\nu = 1146.4$ (P=O) cm^{-1}. SIMS, cation: m/z [$I_{rel.}$(%)] = 575.3 (75.44) [(all)Pd(dpppO)]$^+$; 461.2 (88.75) [dpppO + SH], 429.2 (100) [dpppO + H], 243.2 (46.76) [$Ph_2POC_3H_6$], 201,0 (83.12) [Ph_2PO]. SIMS, anion: m/z [$I_{rel.}$(%)] = 149 (100) [CF_3SO_3]$^-$.

2.3.5. {(η^3-Allyl)[1,2-bis(diphenylphosphino)-ethane-monoxide-κ^2-P,O]palladium(II)} (tolyl-4-sulfonate) [(η^3-allyl)Pd(dppeO)](p-tolSO_3) (13)

Anal. Calc. for $C_{36}H_{36}O_4P_2PdS$ (733.10): C, 58.93; H, 4.95. Found: C, 57.81; H, 5.17. ^1H NMR ($CDCl_3$, 300 MHz, 293 K): [ppm] $\delta =$ 2.34 (s, 3H, CH_3), 2.65–3.00 (br m, 6H, CH_2CH_2, $H^{3,4}$), 4.04 (dd, $J' = 9.3$ Hz, $J'' =$ 14.1 Hz, 1H, H^2), 5.19 (t, $J_{H,H} = J_{H,P} = 6.9$ Hz, 1H, H^1), 5.61 (m, 1H, H^5), 7.08–7.76 (m, 24H, H_{arom}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz, 293 K): [ppm] $\delta = 22.6$ (d, $J = 49.1$ Hz, PPh_2), 36.0 (d, $J = 49.1$ Hz, $P(O)Ph_2$). IR (CH_2Cl_2): [cm^{-1}] $\nu = 3048$ w, 2979 w, 1438 m, 1213 m, 1191 s, 1131 m, 1122 m, 1103 m, 1046 m, 1016 w, 741 s, 730 s, 695 s. SIMS (DTT/DTE/Sul), cation: m/z [$I_{rel.}$(%)] = 561 (20) [(all)Pd(dppeO)]$^+$, 520 (3) [Pd(dppeO)]$^+$, 447 (100) [(dppeO) + SH]$^+$, 443 (8) [Pd(dppeO)−Ph]$^+$, 415 (27) [(dppeO) + H]$^+$, 369 (7), 337 (21), 291 (5) [Ph_2PPd]$^+$, 229 (73) [$Ph_2P(O)CH_2CH_2$]$^+$, 213 (31) [$Ph_2PCH_2CH_2$]$^+$, 201 (11) [Ph_2PO]$^+$, 185 (8) [Ph_2P]$^+$. SIMS (DTT/DTE/Sul), anion: m/z [$I_{rel.}$(%)] = 171 (100) [p–H_3C–C_6H_4–SO_3]$^-$.

2.3.6. (η^3-Allyl)[(1,3-bis(diphenylphosphino)-propane-monoxide-κ^1-P) palladium(II) (tolyl-4-sulfonate) [(η^3-allyl)Pd(dpppO)](p-tolSO_3) (14)

Anal. Calc. for $C_{37}H_{38}O_4P_2PdS$: C, 59.48; H, 5.13. Found: C, 56.93; H, 5.15. ^1H NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 1.81$ (s, broad, 2H, CH_2), 2.64–2.19 (m, 8H, $-Ph_2(P{=}O)CH_2$, CH_2PPh_2, H^3, $-CH_3$[2]), 3.50 (s,broad 1H, H^4), 3.81 (dd, 1H, H^2), 4.90 (t, 1H, H^1), 5.50–5.19 (m, 1H, H^5), 6.97–7.80 (m, 20H, H_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): [ppm] $\delta =$ 13.5 (CH_2), 27.6–25.2 (m, $-Ph_2(P{=}O)CH_2$, CH_2PPh_2), 52.2 (C^3), 81.0 (d, $2J(C,P) = 31$ Hz, C^1), 119.1 (s, C^2), 126.3–132.3 (C_{arom}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): [ppm] $\delta =$ 21.78 ($-PPh_2$), 35.1 ($-Ph_2P{=}O$). IR (nujol mull): $\nu = 1146.4$ (P=O) cm^{-1}.

SIMS, cation: m/z [$I_{rel.}$(%)] = 575 (38.5) [(all)Pd(dpppO)]$^+$; 461 (100.0) [dpppO + SH], 429 (71.7) [dpppO + H], 243 (32.7) [$Ph_2POC_3H_6$], 201.0 (50.9) [Ph_2PO], 147 (37.2) [C_3H_5Pd]; SIMS, anion: m/z [$I_{rel.}$(%)] = 171 (100) [p-H_3C–C_6H_4–SO_3]$^-$.

2.3.7. [Bis(diphenylphosphino)methane-monoxide-κ^2-P,O](acetonitrile)(methyl)palladium(II) tetrafluoroborate (18)

Anal. Calc. For $C_{28}H_{28}BF_4NOP_2Pd$ (649.70): C, 51.76; H, 4.34; N, 2.16. Found: C, 47.20; H, 4.24; N, 2.13. ^1H NMR ($CDCl_3$, 300 MHz, 293 K): [ppm] $\delta = 0.55$ (d, $J = 2.1$ Hz, 3H, $PdCH_3$), 2.30 (s, 3H, $NCCH_3$), 3.71 (dd, $J = 9.6$ Hz, $J = 11.7$ Hz, 2H, CH_2), 7.20–7.38 (m, 12H, H_{arom}), 7.46–7.53 (m, 4H, H_{arom}), 7.67–7.71 (m, 4H, H_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 293 K): [ppm] $\delta = -3.2$ (d, $J = 4.2$ Hz, $PdCH_3$), 2.7 (s, $NCCH_3$), 33.9 (dd, $J = 18.7$ Hz, $J = 64.6$ Hz, CH_2), 118.9 ($NCCH_3$), 126.5–128.9 ($C_{ipso,arom}$), 129.0–133.5 (CH_{arom}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz, 293 K): [ppm] $\delta = 31.4$ (d, $J = 15.0$ Hz, PPh_2), 52.3 (d, $J =$ 15.0 Hz, $P(O)Ph_2$). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 282 MHz, 293 K): [ppm] $\delta = -152.71$ (s, 1F), -152.60 (s, 3F).

The complexes **15**, **16** and **17** show the same ^1H, ^{13}C and ^{31}P data as their analogues bearing tetrafluoroborate as counteranion.

[2] The chemical shift of the allylic proton H^3 was determined with the aid of H,H-COSY (in $CDCl_3$) as: $\delta = 2.45$ ppm (H^3).

*2.3.8. [1,2-Bis(diphenylphosphino)ethane-monoxide-κ²-P,O] (acetonitrile) (methyl)palladium(II) tetrafluoroborate (**19**)*

Anal. Calc. for $C_{29}H_{30}BF_4NOP_2Pd$ (663.73): C, 52.48; H, 4.56; N, 2.11. Found: C, 51.03; H, 4.88; N, 1.55. ^{1}H NMR ($CDCl_3$, 300 MHz, 293 K): [ppm] $\delta = 0.37$ (d, $J = 2.1$ Hz, 3H, $PdCH_3$), 2.18 (s, 3H, $NCCH_3$), 2.49–2.66 (br m, 4H, CH_2CH_2), 7.37–7.58 (m, 16H, H_{arom}), 7.68–7.77 (m, 4H, H_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 293 K): [ppm] $\delta = -1.4$ (d, $J = 2{,}51$ Hz, $PdCH_3$), 2.6 (s, $NCCH_3$), 20.5 (dd, $J = 5.3$ Hz, $J = 31.1$ Hz, CH_2P), 24.0 (d, $J = 68.0$ Hz, $CH_2P(O)$), 117.8 ($NCCH_3$), 127.4–129.5 ($C_{ipso,arom}$), 129.2–133.4 (CH_{arom}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz, 293 K): [ppm] $\delta = 35.7$ (d, $J = 8.7$ Hz, PPh_2), 44.2 (br, $P(O)Ph_2$). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 282 MHz, 293 K): [ppm] $\delta = -153.72$ (s, 1F), -153.77 (s, 3F).

*2.3.9. [1,3-Bis(diphenylphosphino)propane-monoxide-κ²-P,O](acetonitrile) (methyl) palladium(II) tetrafluoroborate (**20**)*

^{1}H NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 0.442$ (s, 3H, CH_3), 1.65 (br, 2H, CH_2), 2.07 (s, 3H, CH_3CN), 2.45 (br, 2H, CH_2PPh_2), 2.69 (br, 2H, CH_2), 7.19–7.75 (m, 20H, H_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz,): [ppm] $\delta = 129.4$–133.6 (C_{arom}), 106 (s, CH_3CN), 26.9 ($Ph_2(P{=}O)CH_2$, CH_2PPh_2), 17.2 (CH_2), 2.78 (s, CH_3CN), −1 ($-CH_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121 MHz,): $\delta = 49.76$ ($-Ph_2P{=}O$), 30.11 ($-PPh_2$); ^{19}F NMR ($CDCl_3$, 282 MHz,): $\delta = -153.6$ (BF_4^-). IR (nujol mull): $\nu = 1153.8$ (P═O) cm^{-1}. SIMS (DTT/DTE/SUL) cation: m/z [$I_{rel.}$(%)] = 549 ($M^+-CH_3CN-BF_4$). SIMS (DTT/DTE/SUL): m/z [$I_{rel.}$(%)] = 87(100) $[BF_4]^-$.

*2.3.10. [Bis(diphenylphosphino)methane-monoxide-κ²-P,O](acetonitrile)(methyl)palladium(II) hexafluoroantimonate (**21**)*

^{1}H NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 0.55$ (d, $J_{H,P} = 2.1$ Hz, 3H, $PdCH_3$), 2.30 (s, 3H, $NCCH_3$), 3.72 (dd, $J_{H,P} = 9.6$ Hz, $J_{H,PO} = 11.7$ Hz, 2H, CH_2), 7.25–7.71 (m, 20H, H_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): [ppm] $\delta = -3.2$ (d, $J_{C,P} = 4.2$ Hz, $PdCH_3$), 2.7 ($NCCH_3$), 33.3 (dd, $J_{C,P} = 18.6$ Hz, $J_{C,PO} = 64.6$ Hz, CH_2), 118.9 ($NCCH_3$), 126.5–128.9 (C_{ipso}), 129.0–133.5 (CH_{arom}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): [ppm] $\delta = 31.39$ (d, $J_{P,P} = 15.0$ Hz, P), 52.32 (d, $J_{P,P} = 15.0$ Hz, PO). IR (nujol mull): $\nu = 1137.0$ (P═O, vs) cm^{-1}. SIMS (NBA), cation: m/z [$I_{rel.}$(%)] = 521 (100) [(dppmO)$PdCH_3]^+$, 506 (18) [(dppmO)$Pd]^+$, 305 (28) [(Ph_2PCH_2)$Pd]^+$, 291 (7) [$Ph_2PPd]^+$, 277 (14), 215 (5) [$Ph_2P(O)CH_2]^+$, 201 (5) [$Ph_2PO]^+$, 199 (5) [$Ph_2PCH_2]^+$, 183 (6), 147 (11). SIMS (NBA), anion: m/z [$I_{rel.}$(%)] = 235 (100) $[SbF_6]^-$.

*2.3.11. [1,2-Bis(diphenylphosphino)ethane-monoxide-κ²-P,O] (acetonitrile) (methyl) palladium(II) hexafluoroantimonate (**22**)*

^{1}H NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 0.38$ (d, $J_{H,P} = 2.4$ Hz, 3H, $PdCH_3$), 2.26 (s, 3H, $NCCH_3$), 2.42–2.55 (m, 4H, CH_2CH_2), 7.40–7.70 (m, 20H, H_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): [ppm] $\delta = -1.4$ (d, $J_{C,P} = 2.5$ Hz, $PdCH_3$), 2.6 ($NCCH_3$), 20.5 (dd, $J_{C,P} = 30.8$ Hz, $J_{C,PO} = 5.0$ Hz, PCH_2), 23.1 (d, $J_{C,PO} = 68.0$ Hz, $P(O)CH_2$), 117.8 ($NCCH_3$), 127.4–128.1 (C_{ipso}), 129.2–133.4 (CH_{arom}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): [ppm] $\delta = 35.88$ (d, $J_{P,P} = 3.5$ Hz, P), 45.34 (br s, PO). IR (nujol mull): $\nu = 1158.3$, 1125.0 (P═O, s) cm^{-1}. SIMS (NBA), cation: m/z [$I_{rel.}$(%)] = 535 (3) [(dppeO)$PdCH_3]^+$, 327 (11), 325 (8), 281 (21), 277 (9), 267 (9), 221 (20), 207 (37), 193 (10), 147 (100), 136 (53). SIMS (NBA), anion: m/z [$I_{rel.}$(%)] = 235 (100) $[SbF_6]^-$.

*2.3.12. [Bis(di-o-tolylphosphino)methane-monoxide-κ²-P,O](acetonitrile)(methyl)palladium(II) hexafluoroantimonate (**23**)*

^{1}H NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 0.51$ (d, $J_{H,P} = 2.1$ Hz, 3H, $PdCH_3$), 2.26, 2.27 (s, 12H, CH_3), 2.28 (s, 3H, $NCCH_3$), 3.42 (br m, 2H, CH_2), 7.04–7.47 (m, 16H, H_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): [ppm] $\delta = -3.0$ ($PdCH_3$), 2.6 ($NCCH_3$), 34.5 (dd, $J_{C,P} = 18.7$

Hz, $J_{C,PO} = 66.0$ Hz, CH_2), 119.0 ($NCCH_3$), 123.2–126.1 (C_{ipso}), 129.8–133.2 (CH_{arom}), 142.6, 144.1 (C_{ipso}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): [ppm] $\delta = 29.70$ (d, $J_{P,P} = 14.6$ Hz, P), 52.22 (br s, PO). IR (nujol mull): $\nu = 1136.3$, 1123.2 (P═O, s) cm^{-1}. SIMS (NBA), cation: m/z [$I_{rel.}$(%)] = 577 (100) $[M-CH_3CN]^+$, 562 (13) [Pd(dtolpmO)]$^+$, 333 (35) $[(tol)_2PCH_2Pd]^+$, 319 (30) $[(tol)_2PPd]^+$, 245 (7), 243 (7) $[(tol)_2P(O)CH_2]^+$, 229 (11) $[(tol)_2PO]^+$, 227 (7) $[(tol)_2PCH_2]^+$. SIMS (NBA), anion: m/z [$I_{rel.}$(%)] = 235 (100) $[SbF_6]^-$.

2.4. Catalytic runs: ethylene oligomerization

Oligomerization of ethylene was carried out in the batch mode with a continuous feed of ethylene into the autoclave, keeping the pressure constant. To this purpose, 75-ml steel autoclaves, equipped with glass inlets and magnetic stirring bars were used. In a typical experiment, 0.1 mmol of the catalyst was dissolved in 10 ml of dichloromethane, and the resulting solution was transferred to the autoclave inlet. Afterwards, the autoclave was pressurized with 30 bars of ethylene. The autoclave was then put to the desired temperature in a preheated oil bath. After the reaction, the autoclave was depressurized and the butenes were collected and weighted at -78°C. The nickel catalyst was separated from the liquid phase by flash distillation of the product solution and condensation at -78°C.

Catalyst activity (TON) and product distribution (linearity, α-content, β-value) were determined by using GC analysis of flash distilled product solution with *n*-nonane as the internal standard. The β-value was deduced from the molar ratios $\alpha = (\text{moles } C_8)/(\text{moles } C_6)$, and $\alpha = 1/(1+\beta)$. Linearity was obtained from C_6-olefins.

2.5. Ethylene / CO copolymerization

Catalytic copolymerization was carried out in 75 ml steel autoclaves equipped with a glass inlet and a Teflon™-coated magnetic stirring bar.

In a typical experiment, 0.1 mmol of the catalyst was dissolved in 10 ml of dichloromethane, and the resulting solution was transferred to the autoclave inlet. Ethylene (30 bars), followed by CO, were pressed into the system for 5 min each, then the autoclave was heated to the desired temperature. After catalysis, the autoclave was cooled in an ice bath to quench the reaction. The polymer was isolated, washed with dichloromethane, dried and weighted. Chemical yield and TON of the catalyst were determined, TON as moles of converted substrate [$m_{polymer}/28$ (g/mol)] per moles of catalyst. The obtained polyketone was analyzed by means of a ^{13}C NMR in 1,1,1,3,3,3-hexafluoro isopropanol (HFIPA).

^{13}C NMR (75 MHz, HFIPA, ext. C_6D_6): $\delta = 212.7$ ppm (C═O), $\delta = 35.9$ ppm (C–C).

A sample of the polymer was analyzed by means of GPC (HFIPA as eluent), M_w = 1 460 000, M_n = 33 582.

Non-soluble samples were analyzed by means of a solid-state NMR that confirmed the polyketone structure [^{13}C NMR (75 MHz, MAS-CP)]: $\delta = 210$ ppm (C═O), $\delta = 36$ ppm (C–C)].

3. Results and discussion

3.1. Synthesis of cationic nickel complexes

The new cationic complexes **1** and **2** have been synthesized in good yields starting from $\{[\eta^3\text{-methallyl})]Ni(Br)\}_2$, ligand and $AgSbF_6$ (Fig. 1).

Since dppaO was not obtained in analytically pure form, a mixture of dppaO/$dppaO_2$ was used for the complex synthesis.

$^{31}P\{^1H\}$ NMR analysis proves the absence of coordinated diphosphine dioxide ($dppaO_2$) in complex **2**. The new complexes were isolated as bright yellow powders and fully characterized by elemental analysis, ^1H-, $^{31}P\{^1H\}$- and $^{13}C\{^1H\}$

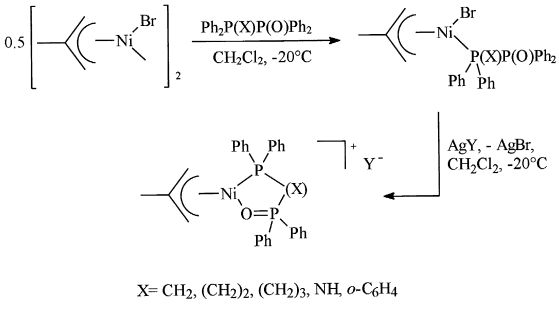


Fig. 1. Synthesis of cationic methallyl nickel complexes. Y = hexafluoroantimonate.

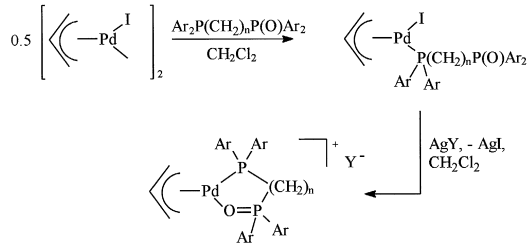


Fig. 2. Synthesis of the cationic allyl palladium complexes. Y = hexafluoroantimonate, tetrafluoroborate, triflate, tosylate; $n = 1$ (dppmO), $n = 2$ (dppeO), $n = 3$ (dpppO); $n = 1$, Ar = *p*-tolyl (dtolpmO).

NMR spectroscopy. Furthermore, IR and SIMS spectra have been recorded.

Similar to the cationic nickel complexes with alkylene bridged biphosphine monoxides, we found that complexes **1** and **2** are P ^O-chelated complexes in methylene chloride solution at room temperature.

Bidentate coordination of the biphosphine monoxide ligands resulted in low field coordination shifts of the phosphine and phosphoryl resonances in $^{31}P\{^1H\}$ NMR, and a shift to lower wavenumbers for the absorption ν(P═O) in the IR-spectra of the complex compared to the free ligand.

While the coordination shifts for the dppbenzO ligand in complex **1** are 14.9 and 29.4 ppm, the coordination shifts in the dppaO complex **2** are 4.9 and 40.6 ppm, respectively.

The assignment of the chemical shifts in the ^{31}P NMR of **2** was done according to the spectra reported for $[(\eta^3\text{-}C_3H_5)Pd(dppaO\text{-}\kappa^2\text{-}P,O)]BF_4$ by Bhattacharyya et al. [32]. Noteworthy, complex **2** possesses fluxional behaviour of the methallyl group at room temperature. Cooling of the probe to 267 K leads to the separation of the allylic resonances.

3.2. Synthesis of cationic palladium complexes

The complexes **10**, **11**, **13**, **14**, **16** and **17** have been synthesized in good yields, starting from 1 eq. of bis-allyl palladium iodide, 2 eq. of biphosphine monoxide, and 2 eq. of the relevant silver salt (Fig. 2).

An important aspect concerning the catalytic activity of these complexes is the coordination mode of the phosphoryl group monitored with the aid of $^{31}P\{^1H\}$ NMR, which is dependent on the anion used in the reaction. As is evident from the experimental data reported, with tetrafluoroborate as anion, the coordination mode is κ^2. When triflate is used as counteranion of the cationic complex, it appears that the phosphoryl group is only partially coordinated to the metal centre.

If tosylate is the counteranion, the coordination mode is clearly κ^1, because of the competition between the stronger coordinating tosylate and the phosphoryl group for the metal centre. With dpppO as ligand, κ^1 coordination can be ascribed to the lower stability of the seven member metallacycle, which is formed when the phosphoryl group is coordinating to the Pd(II) centre. A similar effect has been observed for complexes **6**, **9** and **12**.

The methyl complexes **18**–**23** were synthesized by the reaction of $[(cod)Pd(CH_3)(Cl)]$ adding 1 eq. of ligand and the appropriate silver salt, according to the procedure shown in Fig. 3.

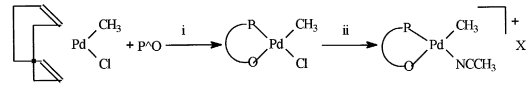


Fig. 3. Synthesis of cationic methyl palladium(II) complexes. (i) RT, dichloromethane, (ii) AgX, CH_3CN/CH_2Cl_2, 0°C; X = hexafluoroantimonate, tetrafluoroborate; P ^ O = biphosphine monoxide ligand.

For these complexes, as it was seen for allyl complexes with analogous ligands, the reaction with the silver salt has the function of exchanging the strongly coordinating chloride with a suitable weakly coordinating counteranion, which has the effect of activating these complexes towards catalysis. The ''vacant coordination site'' is stabilized via the addition of acetonitrile.

Surprisingly, the coordination mode of larger bite P^O ligands, such as dpppO, changes after reacting the neutral methyl complex with silver salt, yielding a cationic complex. $^{31}P\{^{1}H\}$ NMR indicates clearly that only the phosphine coordinates with the palladium in the complex bis-[1,3-bis(diphenylphosphino)propane-monoxide-κ^2-P,O(chloro)(methyl)palladium(II)] $[(CH_3)(Cl)Pd(dpppO)]_2$. This observation can be explained by considering a dimeric structure for the chloro complex (Fig. 4). The reaction of the chloro complex with 1 eq. of silver salt and acetonitrile yields a complex that shows the coordination of P=O functionality.

The complexes **1**–**23** (see Table 1 for the numbering) have been used as catalyst precursors for carbon–carbon linkage reactions. We now want to present and discuss the results of our catalysis runs.

3.3. Ethylene oligomerization: nickel complexes

Cationic organyl nickel complexes with P^O ligands, e.g., diphenylphosphinoalkylcarboxylates, are active as catalysts in the oligomerization of olefins. For ethylene, this type of complex shows only low selectivity to higher linear olefins. This has been ascribed to hemilability of the ligand under catalysis conditions [38].

Table 5
Oligomerization of ethylene with cationic P^O-chelated complexes (0.1 mmol [Ni], 20 ml dichloromethane, 30 bar ethylene, $T = 323$ K, $t = 2$ h)

Run	Complex	TON (mol/mol)	S (linear) (%)	S (α) (%)	β	C_{max}
1	**3**	1692	87.1	64.4	1.03	16
2	**4**	1445	92.0	72.1	1.14	14
3	**5**	397	95.1	88.8	6.52	10
4	**1**	1641	95.9	68.2	0.02	34
5	**2**	2492	87.0	52.6	0.85	18

Therefore, it was of special interest to investigate the new cationic nickel complexes with biphosphine monoxides as P^O-ligands in the oligomerization of ethylene.

From the spectroscopic data of the complexes, a strong oxygen–nickel interaction could be deduced, and a chelate coordination of the ligand is deduced in dichloromethane solution in the absence of further donor ligands.

To elucidate the catalytic behavior of these complexes in the oligomerization of ethylene, the cationic complexes **1**–**5** with biphosphine monoxide ligands have been used in ethylene oligomerization. The results are reported in Table 5.

The complexes **1**–**5** are efficient catalyst precursors for the oligomerization of ethylene to linear, higher α-olefins. While selectivities to linear olefins are very high, the lower selectivity to α-olefins shows that the cationic complexes **1**–**5** are also efficient catalysts for the isomerization of α-olefins to internal olefins. Still, the selectivities to linear α-olefins are very impressive, and to the best of our knowledge, the results obtained with complexes **1**–**5** in terms of selectivity are the best reported for cationic

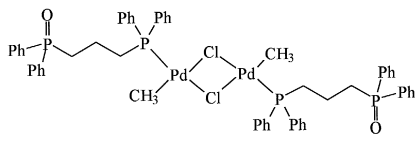


Fig. 4. Alleged structure for the complex $[(CH_3)(Cl)Pd(dpppO)]_2$.

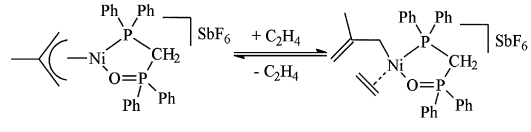


Fig. 5. Proposed coordination mode of ethylene to nickel in complex **3**.

Table 6
Catalytic results with in situ-formed nickel complexes obtained by the reaction of (η^3-methallyl)Ni(cod)SbF_6 and 1 eq. of ligand

Run	*n*(ligand): *n*(complex) (mol/mol)	TON (mol/mol)	*S* (linear) (%)	*S* (α) (%)	β	C_{max}
1	0	610	65.3	7.0	6.00	8
2	1.03 dppmO	1724	89.7	71.6	1.08	16
3	1.03 dppeO	1470	94.5	83.9	1.18	14
4	1.09 dpppO	1910	63.0	16.3	3.20	10
5	1.06 dppbenzO	2295	96.5	67.6	0.12	34
6	1.12 dppaO	1478	89.2	79.6	0.95	16

Table 8
Addition of monodentate phosphines to a solution of complex **1**

Run	*n*(Ligand): *n*(Ni) (mol/mol)	TON (mol/mol)	*S* (linear) (%)	*S* (α) (%)	β	C_{max}
1	0	1641	95.9	68.2	0.02	34, waxes
2	0.50 PPh_3	861	99.0	90.6	0.05	waxes
3	1.06 PPh_3	1475	98.4	96.4	1.74	14
4	2.07 PPh_3	886	97.0	94.5	6.60	10
5	4.09 PPh_3	264	98.2	95.8	6.87	8
6	1.09 PCy_3	645	93.6	82.7	0.04	waxes
7	2.09 PCy_3	138	95.4	87.1		14

P^O-chelated nickel complexes so far. The comparison with selectivities reported by Ecke and Schulz for phosphinocarboxylates as neutral P^O-ligands shows that linearities, as well as α-contents of the C_6-olefins, are dramatically increased through the use of biphosphine monoxides as P^O-ligands [18,19]. We ascribe the good selectivities to a very stable nickel–oxygen bond and, therefore, a chelate coordination of the P^O-ligand, similar to chelate coordination of anionic ligands in SHOP-type catalysts.

The catalysis results can best be rationalised by the assumption that the chelate coordination remains intact throughout the course of catalysis. Thus, ethylene is not replacing the phosphoryl group but is coordinating and inserting into the organyl group without the cleavage of the nickel–oxygen bond (Fig. 5).

The support for the proposal in Fig. 5 stems from the following considerations.

Activities of the complexes **1**–**5** follow the same trend as for neutral complexes with anionic chelate P^O-ligands. The activity of complexes **1**–**5**, as well as the maximum chain length of product olefins as a parameter for oligomerization grade, increases with decreasing chelate ring size of the complex. While the dppmO complex is yielding oligomers up to C_{16}, the dpppO complex yields only short-chained olefins. Assuming that only the square-planar nickel hydride is active in the oligomerization, the chain length of the built product will depend on the chelate ring size, because larger chelate rings will favour tetrahedral configuration.

The closer the coordination geometry to the square-planar coordination, the higher the oligomerization number. Furthermore, the higher the rigidity of the ligand backbone, the higher the activation energy for a β-elimination via a penta-coordinated species and the higher the oligomerization number. This was proven by synthesising and applying a cationic complex with dppbenzO as P^O ligand. The slightly lowered activity of the dppbenzO complex in comparison with the dppmO complex can be explained invoking a diffusion-controlled reaction due to the resulting slurry of waxes that limits further conversion of ethylene to

Table 7
Distribution of C_6-isomers for reactions reported in Table 5

Run	3-Methyl-1-pentene	1-Hexene	2-Ethyl-1-butene	*Cis* and *trans* 3-hexene	3-Methyl-2-pentene	*Cis* and *trans* 2-hexene
1	1.5	64.3	10.6	5.4	0.9	17.5
2	1.5	71.6	8.2	4.0	0.6	14.1
3	1.4	70.1	0	3.2	0	25.4
4	1.4	67.6	0	3.3	2.1	25.7
5	3.2	7.0	0.9	19.1	30.5	39.3

Table 9
Comparison with hemilabile P ^O ligands by in situ catalysis with {(η^3-methallyl)(η^4-1,5-cyclooctadiene)nickel(II)}hexafluoroantimonate

Run	*n*(Ligand): *n*(Ni) (mol/mol)	TON (mol/mol)	*S* (linear) (%)	*S* (α) (%)	*β*	C_{max}
1	1.05 dppanis	1252	26.8	1.1	12.98	8
2	1.04 dppres	1076	32.8	1.6	21.22	8
3	1.06 dppOPh	1712	25.9	0.8	9.87	8
4	1.11 dppacet	661	39.4	2.4	4.38	10
5	1.09 dppbald	1952	45.7	7.6	9.87	10
6	1.08 dpppaEt	552	38.4	4.0	9.36	8
7	1.04 dppbenzaMe	3192	43.7	5.2	5.38	10

oligomers. At this time, it still remains unclear whether the good selectivities are only a result of high electron density at the nickel centre through effective bonding of the donor group or whether the selectivity is a result of effective shielding of the nickel through the phenyl-substituted phosphoryl group as well.

The results with defined complexes could be supported through applying in situ catalysts starting from {[η^3-methallyl)]Ni(cod)}SbF_6 and a stoichiometric amount of ligand. After the preformation of the catalyst and the substitution of 1,5-cyclooctadiene through the P ^O ligand, 1,5-cyclooctadiene has no effect on the catalyst performance in comparison to the defined complexes **1**–**4**, as can be deduced from the results in Table 6.

The difference in catalytic activity and selectivity from dpppO complex **5** and the analogous in situ system {[η^3-methallyl]Ni(cod)}SbF_6/dppO (entry 4) cannot be easily explained.

The dppaO complex shows remarkably high activity compared to the alkylene and phenylene bridged ligands. Compared to neutral complexes, cationic complexes seem to inherit a high activity but a lower oligomerization number. Table 7 describes the selectivity for the C_6-isomers.

Addition of different amounts of monodentate phosphine to a solution of dppbenzO complex **1** (Table 8) had the expected effect of lowering the oligomerization grade and the catalyst activity. Remarkably, we still observed catalytic activity after addition of 2 eq. PCy_3 to complex **1**. Despeyroux [39] and Müller et al. [40] reported the isolation of catalytically inactive, neutral nickel hydrides after the addition of 2 eq. of PCy_3 to an active oligomerization system. It seems likely that reaction pathways are different for cationic and neutral complexes. Probably, for oligomerization with cationic complexes, a higher coordinated species, still possessing catalytic activity, can be built. The outstanding performance of biphosphine monoxide ligands is shown in comparison to both, defined complexes and in situ catalysts with other P ^O-ligands (Table 9).

While nickel complexes with biphosphine monoxides show excellent selectivities to higher α-olefins, application of other neutral P ^O-ligands led only to catalyst systems with poor selectivities. Among the used ligands are also the diphenylphosphinoalkylcarboxylates reported by Ecke and Schulz. While the selectivities to linear olefins are in the range of 25–50%, the α-olefins contents are drastically reduced.

Table 10
Olefin oligomerization with cationic allyl and methyl palladium complexes under used conditions: 30 bar const., 20 ml CH_2Cl_2, 2 h, 70°C

Run	Ligand	All/Me, anion	Cat. mmol	TOF (1/h)	*S* (linear)	*S* (1-hexene)	C_{max}	C_4 (mass%)	C_6 (mass%)	C_8 (mass%)	C_{10} (mass%)	C_{12} (mass%)	*β*
1	dppmO	All, SbF_6	0.040	7794	75.8	44.6	12	65.9	24.7	7.1	1.8	0.5	3.64
2	dtolpmO	All, SbF_6	0.046	4228	81.2	45.6	12	77.6	17.0	4.3	0.9	0.2	4.30
3	dppeO	All, SbF_6	0.046	4747	52.5	14.7	10	83.7	13.7	2.3	0.3	–	6.99
4	dppmO	Me, SbF_6	0.050	8974	73.5	30.2	12	65.3	24.6	7.7	1.9	0.5	3.25
5	dtolpmO	Me, SbF_6	0.050	5012	77.7	15.1	10	85.7	11.8	32.2	0.3	–	6.23
6	dppeO	Me, SbF_6	0.050	5512	49.3	0.6	10	80.6	16.8	2.3	0.3	–	8.92

Table 11
Ethylene/CO copolymerization catalysed by allyl palladium complexes
Conditions: ethylene 30 bars, CO 30 bars, solvent dichloromethane (10 ml), reaction temperature 50°C.

Run	Complex	mol 10^{-4}	*m* ethylene (g)	*m* CO (g)	Conversion CO%	TON	*m* polymer (g)
1	(**12**) (all)Pd(dppmO)Tos	1	4.60	2.59	9.3	171	0.48
2	(**9**) (all)Pd(dppmO)Tf	1.01	4.60	2.72	39.5	760	2.15
3	(**6**) (all)Pd(dppmO)BF_4	0.95	3.91	2.96	45.0	1000	2.66
4	(**13**) (all)Pd(dppeO)Tos	0.99	4.80	2.40	5.8	101	0.28
5	(**10**) (all)Pd(dppeO)Tf	0.99	4.71	2.66	14.3	274	0.76
6	(**7**) (all)Pd(dppeO)BF_4	0.99	4.58	2.48	15.7	281	0.78
7	(**14**) (all)Pd(dpppO)Tos	1.00	3.71	2.65	1.0	21	0.06
8	(**11**) (all)Pd(dpppO)Tf	1.00	4.25	2.58	4.4	82	0.23
9	(**8**) (all)Pd(dpppO)BF_4	1.00	3.10	2.65	14.1	268	0.75

Both the oligomerization grades and the resulting C_{max} are similar to those obtained with monodentate phosphines, e.g., PPh_3. Therefore, we conclude that these P ^O-ligands behave as hemilabile ligands under catalysis conditions, in contrast to the biphosphine monoxides.

To further investigate the chelate control, we tried to synthesize the complex {(η^3-methallyl)Ni(Ph_3P)($Ph_2MeP(O)$)}SbF_6. Attempts to fully characterize the complex failed due to its low stability. Nevertheless, we applied the in situ complex to catalysis without further purification.

3.4. Oligomerization of ethylene catalysed by Pd(II) complexes

The influence of chelating ligands on ethylene oligomerization applying Pd-complexes is shown in Table 10. With dppmO, the best activities are achieved while once more, the effect of ring size of the chelating complex to catalysis is obvious from the results obtained. Five ring chelates (dppmO, dtolpmO) show higher selectivities to linear, as well as to alpha olefins than six-membered rings do (dppeO). β-values of Schulz–Flory distribution are rising in the row: dppmO < dtolpmO < dppeO, but major products obtained are butenes (65–85%), while the amount of decenes or dodecenes is negligible. The difference in electronic and steric effects of dtolpmO in comparison to dppmO leads to increased selectivity to linear products although turnover frequencies are much lower.

Moreover, the cationic methyl complexes are more active than their allyl analogues. The turnover frequencies are about 15% lower when using the allyl precursor. This can be ascribed to the activation energy of the starting step to form the catalytic active species. The selectivity to linear ethylene oligomers are in the same range, but still a little bit higher when using allyl precursor complexes.

In addition, the isomerization activity of methyl complexes (due to selectivity to 1-hexene) is much higher than that of the correspondent allyl complexes. This can only be explained with the presence of 1 eq. acetonitrile from the starting compound in the case of methyl complexes. Another explanation for the lower amount of 1-hexene might be the incorporation

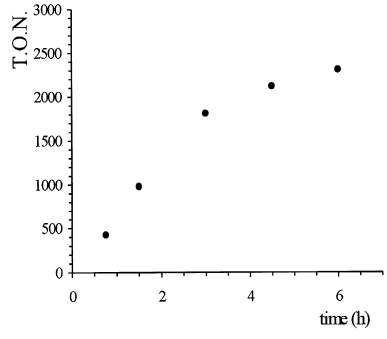


Fig. 6. Activity of complex **6** as a function of reaction time in the ethylene/CO copolymerization.

Table 12
Ethylene/CO copolymerization
Conditions: ethylene 30 bars, CO 30 bars, solvent dichloromethane (10 ml), reaction time 15 h.

Entry	Complex	mmol	Ethylene (g)	*m* CO (g)	Conversion CO%	TON	*m* polymer (g)
1	**6** (all)Pd(dppmO)BF_4	0.099	5.04	2.77	92	1825	5.11
2	**6** (all)Pd(dppmO)BF_4	0.049	4.88	3.14	86	3915	5.40
3	**6** (all)Pd(dppmO)BF_4	0.025	4.93	2.93	53	4455	3.13
4	**18** $(CH_3)(CH_3CN)$Pd(dppmO)BF_4	0.098	5.31	2.77	96	1950	5.34
5	**18** $(CH_3)(CH_3CN)$Pd(dppmO)BF_4	0.049	5.62	2.92	84	3320	4.60
6	**18** $(CH_3)(CH_3CN)$Pd(dppmO)BF_4	0.025	5.50	2.98	54	4519	3.21

of already produced α-olefins as substrate in the catalytic cycle.

Another effect of the strong donor acetonitrile is its competition with ethylene or product olefins for coordination on palladium, and the consequent higher chain transfer rates observed in catalysis with methyl complexes. The same effect is observed in our presented nickel catalysed ethylene oligomerization when phosphines are added to the solution [41].

3.5. Alternating copolymerization of ethylene and carbon monoxide with palladium(II) complexes

In order to perform a first screening of catalytic activity, the complexes **6**–**14** were employed in the catalytic copolymerization of ethylene and CO at 50°C. The results are summarized in Table 11.

Two features appear from these results: the dppmO complexes combined with BF_4^- are the most active ones. An explanation of this behaviour can be given if it is assumed that dppmO, dppeO and dpppO form five-, six- and seven-membered metallacycles with Pd(II). The higher stability of the five terms metallacycle that is formed in the dppmO complexes can be invoked to justify that the catalyst is more stable and, therefore, more active, whereas dppeO and dpppO complexes tend to be reduced to Pd(0) under reaction conditions.

The effect of the counteranion is dependent upon its coordination ability. It should increase in the order: tosylate, triflate, tetrafluoroborate; this explains the higher activity of the complexes bearing BF_4^- as anion. The effect of temperature was analyzed by setting analogous experiments at different temperature. The highest activity was reached at 80°C; decomposition of the catalyst is invoked for the drop in activity above 80°C.

Based on the conclusions drawn from this first screening, we decided to continue our investigations with the most active complex, namely {(all)Pd(dppmO)}BF_4 (**6**) at the highest temperature possible, i.e., 80°C.

In order to assess if an induction period was necessary to start the catalytic cycle, five different experiments were set under the same conditions just varying the reaction time. The results are shown in Fig. 6, and prove that no induction period is required to trigger the catalytic cicle. The observed change in slope in the curve may be due to the polymerization reaction turning under diffusion control above 3 h.

The amount of the catalyst employed was also subject to optimisation. We observed a drop in catalytic activity for **6** above 0.05 mmol. This is obviously due to the decomposition of

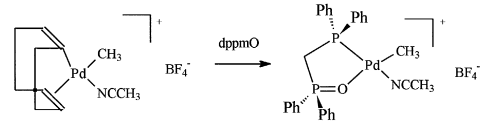


Fig. 7. In situ formation of the chelate complex (dppmO)-Pd$(CH_3)(NCCH_3)$ BF_4.

Table 13
Ethylene/CO copolymerization
Conditions: ethylene 30 bars, CO 30 bars, solvent dichloromethane (10 ml); reaction temperature 80°C; reaction time 15 h. For reactions 4, 5, and 6, the precursor complex is (cod)Pd($NCCH_3$)(CH_3)BF_4 (0.1 mmol).

Entry	Complex or ligand	mmol	*m* ethylene (g)	*m* CO (g)	Conversion CO%	TON	*m* polymer (g)
1	**18** (CH_3)(CH_3CN)Pd(dppmO)BF_4	0.099	5.04	2.77	92	1825	5.11
2	**19** (CH_3)(CH_3CN)Pd(dppeO)BF_4	0.1	4.96	2.77	29	575	1.61
3	**20** (CH_3)(CH_3CN)Pd(dpppO)BF_4	0.099	4.68	2.69	30	566	1.58
4	dppmO	0.098	4.90	2.60	95	1793	4.92
5	dppeO	0.098	5.30	2.83	28	598	1.65
6	dpppO	0.099	5.21	2.73	18	473	1.32

the catalyst via reduction of the Pd(II) to Pd(0) in the reaction medium.

A further reaction screening was done to establish the activity of the methyl complexes **18**, **19** and **20**. The question arising was whether an allyl-Pd-group or a methyl-Pd-group gives different results. Data for this screening are collected in Table 12.

We found that it is possible to activate the copolymerization reaction, not only through the preformed complexes previously described, but also through the in situ formed catalysts, by the use of particular precursor complexes like the methyl complex [(cod)Pd($NCCH_3$)(CH_3)]BF_4. When this complex is reacted with an eq. of bidentate ligand, the coordinated diolefin cyclooctadiene is scavenged from the complex itself, giving rise to the catalyst precursor, which is responsible for the copolymerization reaction (Fig. 7).

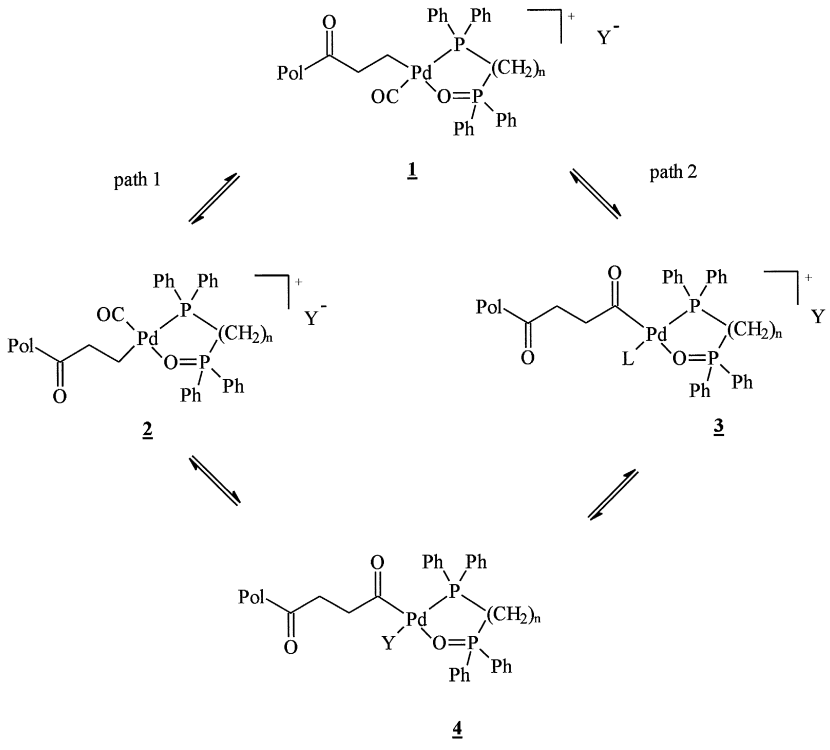


Fig. 8. Alleged chain growth pathways for CO migratory insertion in the ethylene/CO copolymerization with palladium P ^PO complexes (Pol: growing polyketone; Y: counteranion; L: solvent).

It is evident from Tables 12 and 13 that chelate ring size influences catalytic activity (in the order dppmO > dppeO > dpppO) and that methyl complexes do not exhibit a higher catalytic activity than their allyl analogues. This can be rationalised in terms of the activation step, which is faster than the chain growth in the ethylene/CO copolymerization.

The self-explanatory mechanism of the activation of ethylene/CO copolymerization catalysed by hemilabile complexes of Pd(II) was thoroughly investigated by Mecking and Keim [42] and is shown in Fig. 8.

In comparison to Shell's results [43], the activity of our complexes is lower. A possible explanation could lie in the ''soft–hard'' nature of the ligand. Let us, for example, consider the CO insertion in the growing chain. It is widely accepted that CO migratory insertion into a Pd–alkyl bond is favoured if the alkyl group bears a partial negative charge and the coordinated CO, on the other hand, bears a partial positive charge (for a complete review, see Ref. [44]). This is the case if a phosphorous atom is *trans* to the alkyl growing chain, and a P═O group is *trans* to the coordinated CO. Species **1** in Fig. 8, which represents the starting species for pathway 1 or 2, shows the growing chain *cis* to phosphorous and CO *trans* to it, a situation unfavourable for insertion because the alkyl growing chain is *cis* to the phosphorous atom and *trans* to the oxygen atom. The starting species **1** has to isomerize to **2** before migratory insertion to yield **4** can happen. This isomerization is an energetically unfavourable process and would lead to slower insertion rates with respect to the P ^P or N ^N Pd(II) complexes, where isomerization is not needed. Path 2 shows the kinetically unfavoured direct migration that leads to the thermodynamically stable acyl product **3**, which quickly rearranges into **4**. Therefore, the rearrangement barrier that the complex has to undergo in path 1, or the kinetic barrier in the migratory step in path 2, can account for the slower growing rate of the copolymer in the CO insertion step. A similar effect was observed by Vrieze et al. [45] in the course of the study of the carbonylation reaction of norbornene with Pt(II) or Pd(II) complexes with phosphino-amines as ligands. It is safe to assume that similar effects might play a role in the ethylene insertion in the Pd–acyl bond.

4. Conclusions

New nickel(II) and palladium(II) complexes with biphosphine monoxide ligands have been synthesized and characterized. Cationic organyl nickel complexes with biphosphine monoxides are very efficient catalysts in the oligomerization of ethylene towards higher α-olefins. Cationic palladium(II) complexes exhibit activity towards the oligomerization of ethylene and the copolymerization of ethylene and CO.

Acknowledgements

Financial support from the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen (Katalyseverbund NRW) and from the Deutsche Forschungsgemeinschaft is gratefully acknowledged. Cosimo Francesco Nobile, Gian Paolo Suranna and Piero Mastrorilli gratefully acknowledge Italian MURST and CNR for financial support.

References

[1] G. Wilke, Angew. Chem. 100 (1988) 189.
[2] W. Keim, Angew. Chem., Int. Ed. Eng. 29 (1990) 235.
[3] W. Keim, F.H. Kowaldt, R. Goddard, C. Krüger, Angew. Chem. 90 (1978) 493.
[4] A. Bader, E. Lindner, Coord. Chem. Rev. 108 (1991) 27.
[5] W. Kaminsky, M. Arndt, in: B. Cornils, W. Herrmann (Eds.), Applied Homogeneous Catalysis, VCH, Weinheim, 1996.
[6] G. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem. 111 (1999) 448.
[7] G.W. Parshall, S.D. Ittel, Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes, 2nd edn., Wiley-Interscience, New York, 1992.
[8] C.M. Killian, L.K. Johnson, M. Brookhart, Organometallics (1997) 2005.

[9] L.K. Johnson, C.M. Killian, M. Brookhart, J. Am. Chem. Soc. 117 (1995) 6414.
[10] J. Skupinska, Chem. Rev. 91 (1991) 613–648.
[11] W. Keim, Angew. Chem. 102 (1990) 251.
[12] C.M. Killian, L.K. Johnson, M. Brookhart, Organometallics 16 (1997) 2005, (and references therein).
[13] B.L. Small, M. Brookhart, JACS 129 (1998) 7143, (and references therein).
[14] W. Keim, B. Hoffmann, R. Lodewick, M. Peuckert, G. Schmitt, J. Fleischhauer, U. Meier, J. Mol. Catal. 6 (1979) 79.
[15] D. Vogt, in: B. Cornils, W. Herrmann (Eds.), Applied Homogeneous Catalysis, VCH, Weinheim, 1996.
[16] M.C. Bonnet, F. Dahan, A. Ecke, W. Keim, R.P. Schulz, I. Tkatchenko, J. Chem. Soc., Chem. Commun. (1994) 615.
[17] D. Matt, M. Huhn, J. Fischer, A. De Cian, W. Kläui, I. Tkatchenko, M.C. Bonnet, J. Chem. Soc., Dalton Trans. (1993) 1173.
[18] A. Ecke, Dissertation, RWTH Aachen, 1995
[19] R.P. Schulz, Dissertation, RWTH Aachen, 1993.
[20] Chem. Week 1 (1995) 22.
[21] F.Y. Xu, J.C.W. Chien, Macromolecules 26 (1993) 3485.
[22] A. Sen, Adv. Polym. Sci. 73/74 (1986) 126.
[23] P. Margl, T. Ziegler, J. Am. Chem. Soc. 118 (1996) 7337.
[24] P. Margl, T. Ziegler, Oganometallics 15 (1996) 5519.
[25] W. Keim, H. Maas, S. Mecking, Z. Naturforsch. 50b (1995) 430.
[26] S. Mecking, W. Keim, Organometallics 15 (1996) 2650.
[27] G.J.P. Britovsek, W. Keim, S. Mecking, D. Sainz, T. Wagner, J. Chem. Soc., Chem. Commun. (1993) 1632.
[28] W. Keim, R.P. Schulz, J. Mol. Catal. 92 (1994) 21.
[29] G.J.P. Britovsek, K.J. Cavell, M.J. Green, F. Gerhards, B.W. Skelton, A.H. White, J. Organomet. Chem. 533 (1997) 201.
[30] I. Brassat, U. Englert, W. Keim, D.P. Keitel, S. Killat, G.P. Suranna, R. Wang, Inorg. Chim. Acta 280 (1998) 150.
[31] N.A. Bondarenko, M.V. Rudomino, E.N. Tsvetkov, Synthesis (1991) 125.
[32] P. Bhattacharyya, A.M.Z. Slawin, M.B. Smith, J.D. Woollins, Inorg. Chem. 35 (1996) 3675.
[33] G.P.C.M. Dekker, A. Buijs, C. Elsevier, K. Vrieze, P.W.N.M. Van Leeuwen, W.J.J. Smeets, A.L. Spek, V.F. Wang, C.H. Stam, Organometallics 11 (1992) 1937.
[34] G. Wilke, DOS 1,194,417-10.06.1965.
[35] R.B.A. Bardy, I. Tkatchenko, J. Chem. Soc., Chem. Commun. (1981) 49.
[36] D.L. Tibbetts, T.L. Brown, J. Am. Chem. Soc. 91 (1969) 1108.
[37] R.E. Rülke, J.M. Ernsting, A.L. Spek, C.J. Elsevier, P.W.N.M. van Leeuwen, K. Vrieze, Inorg. Chem. 32 (1993) 5769.
[38] M.C. Bonnet, F. Dahan, A. Ecke, W. Keim, R.P. Schulz, I. Tkatchenko, J. Chem. Soc., Chem. Commun. (1994) 615.
[39] B. Despeyroux, PhD Thesis, Aachen, 1981.
[40] U. Müller, W. Keim, C. Krüger, P. Betz, Angew. Chem. 101 (1989) 1066.
[41] I. Brassat, Dissertation, RWTH Aachen, 1998.
[42] S. Mecking, W. Keim, Organometallics 15 (1996) 2650.
[43] E. Drent, J.A.M. vanBroekhoven, P.H.M. Budzelaar, Recl. Trav. Chim. Pays-Bas 115 (1996) 263, and refs. therein.
[44] K. Cavell, Coord. Chem. Rev. 155 (1996) 209.
[45] K. Vrieze, P.V. Leeuwen et al., Organometallics 11 (1992) 1937.