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Catalytic activity of cationic diphospalladium(II) complexes in the alkene/CO copolymerization in organic solvents and water in dependence on the length of the alkyl chain at the phosphine ligands

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Dedicated to Professor Reinhard Schmutzler on the occasion of his 65th birthday

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Abstract

A series of diphos ligands $CH_2(CH_2PR_2)_2$ (**1a**–**x**) (**a**–**g**: $R = (CH_2)_nOH$, $n = 1$, 3–8; **h**–**k**: $R = (CH_2)_nCH(CH_2OH)_2$, $n = 3$–6; **l**–**u**: $R = C_nH_{2n+1}$, $n = 1$–8, 10, 14; **v**–**x**: $R = CH(CH_3)_2$, $(CH_2)_2CH(CH_3)_2$, $(CH_2)_3CH(CH_3)_2$, (Scheme 1), provided with functionalities of different polarity, was prepared photochemically by hydrophosphination of the corresponding 1-alkenes with $H_2P(CH_2)_3PH_2$ or reaction of Grignard reagents with $Cl_2P(CH_2)_3PCl_2$. The water-soluble palladium complexes $[(R_2P(CH_2)_3PR_2)Pd(OAc)_2]$ (**2a**–**k**) were obtained by reaction of $Pd(OAc)_2$ with the ligands **1a**–**k** in ethanol–acetonitrile. Treatment of $PdCl_2(NCC_6H_5)_2$ with **1l**–**x** afforded the dichloropalladium(II) complexes $[(R_2P(CH_2)_3PR_2)PdCl_2]$ (**3l**–**x**). Upon chloride abstraction with $AgBF_4$ in dichloromethane–acetonitrile the dicationic palladium(II) complexes $[(R_2P(CH_2)_3PR_2)Pd(NCCH_3)_2][BF_4]_2$ (**4l**–**x**) are formed. The structure of **4n** ($R = n$-Pr) was investigated by an X-ray structural analysis. In particular the water-soluble complexes **2c**–**k** proved to be highly active in the carbon monoxide/ethene copolymerization under biphasic conditions (water–toluene). In the presence of an emulsifier and methanol as activator the catalytic activity increased by a factor of about three. Also higher olefins could be successfully incorporated into the copolymerization with CO and the terpolymerization with ethene and CO. The catalytic activity of the dicationic complexes **4l**–**x** in the propene or 1-hexene/CO copolymerization strongly depends on the length of the alkyl chain R. At 25°C a maximum is achieved in the case of **4q** ($R = n$Hex) which is five times more active than the corresponding catalyst with the dppp-ligand. This maximum is shifted to **4t** ($R = n$-$C_{10}H_{21}$) if the temperature is raised to 60°C. The 1-alkene/CO copolymers are distinguished by their regioregular microstructure and their ultra high molecular weights. Compared to the sulfonated dppp-SO_3 catalyst the water-soluble complexes **2c**,**e**,**f**,**h** are responsible for a higher 1-hexene incorporation in the terpolymerization of ethene with 1-hexene and CO. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Palladium complexes; Water solubility; Homogeneous catalysis; Copolymerization; Polyketones

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1. Introduction

The palladium catalyzed strictly alternating copolymerization of alkenes with carbon monoxide still attracts considerable attention. This interest stems from the easy and cheap access of the starting materials, a plausible and well investigated reaction mechanism [1], the polymers engineering properties [2], the possibility of further derivatization of the carbonyl group [3], and from the potential utility of the polyketones as photodegradable materials [4]. Commonly the copolymerization is catalyzed by cationic palladium(II) com-

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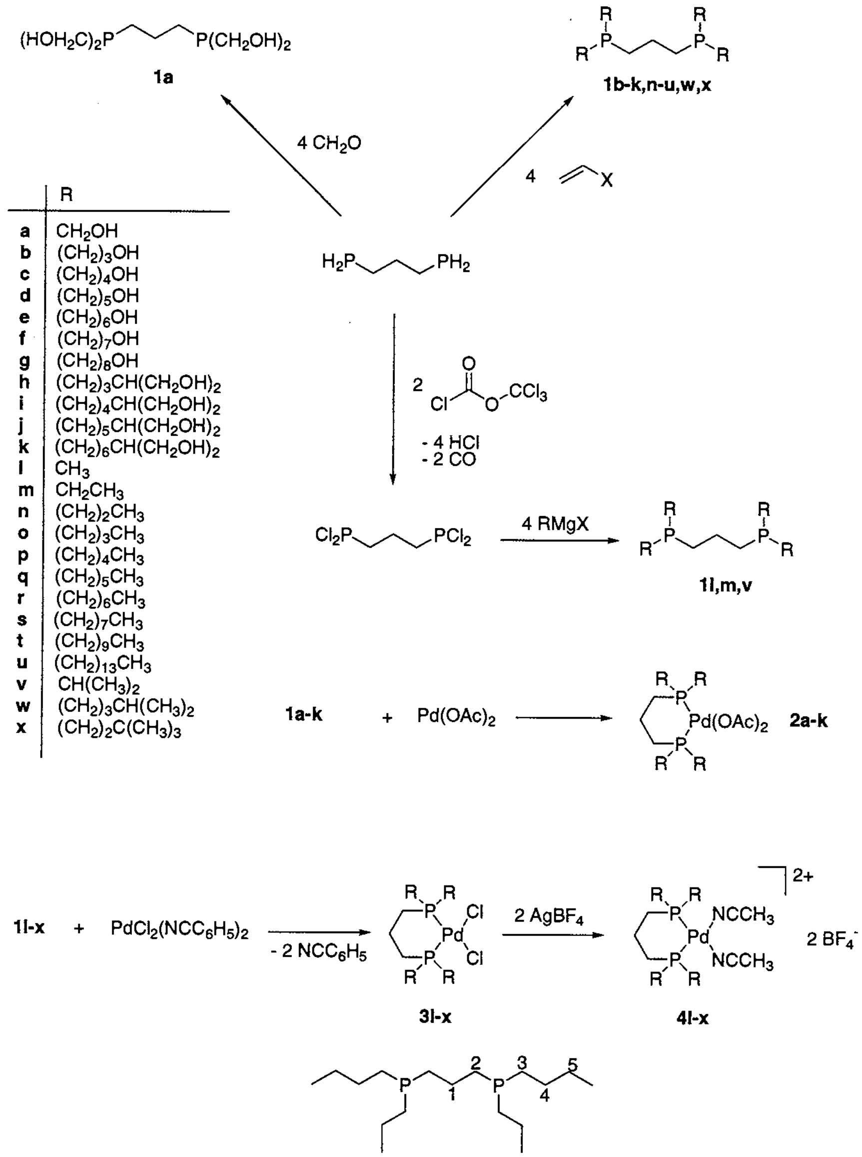

	R
a	CH_2OH
b	$(CH_2)_3OH$
c	$(CH_2)_4OH$
d	$(CH_2)_5OH$
e	$(CH_2)_6OH$
f	$(CH_2)_7OH$
g	$(CH_2)_8OH$
h	$(CH_2)_3CH(CH_2OH)_2$
i	$(CH_2)_4CH(CH_2OH)_2$
j	$(CH_2)_5CH(CH_2OH)_2$
k	$(CH_2)_6CH(CH_2OH)_2$
l	CH_3
m	CH_2CH_3
n	$(CH_2)_2CH_3$
o	$(CH_2)_3CH_3$
p	$(CH_2)_4CH_3$
q	$(CH_2)_5CH_3$
r	$(CH_2)_6CH_3$
s	$(CH_2)_7CH_3$
t	$(CH_2)_9CH_3$
u	$(CH_2)_{13}CH_3$
v	$CH(CH_3)_2$
w	$(CH_2)_3CH(CH_3)_2$
x	$(CH_2)_2C(CH_3)_3$

Scheme 1.

plexes, provided with bidentate phosphorus and nitrogen ligands [5] and weakly coordinating anions [6]. In particular diphosphines with a hydrocarbon backbone consisting of three methylene groups belong to the most active catalysts [5,7]. Late transition metal complexes are suitable for the copolymerization of polar and non-polar monomers. A great variety of olefins [8] and imines [9] were employed and even carbon monoxide was replaced by other polar building blocks [10].

Steric and electronic properties of the catalyst exert strong influence in metal mediated polymerizations. In the polymerization of olefins with β-diiminenickel(II) and palladium(II) complexes bulky substituents are needed to suppress chain transfer and termination reactions [11]. Gibson et al. showed that cobalt(III) and iron(II) complexes with steric demanding tridentate nitrogen donors are suitable for the polymerization of ethylene, while less bulky ligands are responsible for oligomers [12]. Moreover the microstructure of the resulting polymers can be controlled by the catalyst. In the copolymerization of propene with carbon monoxide the regio- and stereoregularity of the polyketones is dependent on the kind of the substituent attached to the phosphorus donor. With $[(dppp)Pd(NCMe)_2][BF_4]_2$ (dppp = 1,3-bis(diphenylphosphino)propane) regioirregular materials are obtained, whereas alkyl substituents lead to almost perfectly head-to-tail connected units [13]. Recently optically active polyketones were prepared by using chiral palladium(II) complexes [13b,14]. Finally the ligand offers the possibility to adapt the solubility of the catalyst for different media [15]. The present work is devoted to an efficient ligand synthesis, which offers an easy access to diphos ligands with phosphorus attached alkyl substituents of different chain length. These alkyl groups contain terminal polar or non-polar functions. Palladium(II) complexes with these ligands were applied in the copolymerization of carbon monoxide with ethene and different α-olefins in water, organic solvents, and in a biphasic system with and without emulsifiers. By variation of the kind of surfactants, the electronic and steric factors of the catalysts and the reaction temperature, the impact on the catalytic activity and the molecular weights of the polyketones were studied and optimized.

2. Results and discussion

2.1. Synthesis of the diphos ligands *1a–x* and diphospalladium(II) complexes *2a–k*, *3l–x*, and *4l–x*

With some modifications the diphos ligands **1b**–**k**,**n**–**u**,**w**,**x** were prepared according to a procedure described by Maier [16]. An excess of the corresponding olefin was photochemically hydrophosphinated with the diprimary phosphine $H_2P(CH_2)_3PH_2$ (Scheme 1). This convenient synthesis is nearly quantitative and simplifies the purification of the products. Ligand **1a** was only mentioned in a patent and is available by reaction of four equivalents of formaldehyde with $H_2P(CH_2)_3PH_2$ [17]. Finally the ligands **1l**,**m**,**v** were made accessible by treatment of $Cl_2P(CH_2)_3PCl_2$ [18] with the Grignard reagents RMgX. The tetrachlorodiphosphine was obtained in high yields from $H_2P(CH_2)_3PH_2$ and trichloromethyl chloroformate. All phosphines are colorless, air-sensitive and oily (**1b**–**t**,**v**,**w**) or solid (**1a**,**u**,**x**) products. Whereas the hydroxyalkyl functionalized species **1a**–**k** are soluble in alcohols and with the exception of **1f**,**g**, also in water, **1l**–**x** are soluble in all common organic solvents. Their characterization was carried out by means of MS, IR, and NMR spectroscopy (see Section 4).

Upon reaction of palladium(II) acetate with the phosphines **1a**–**k** in mixtures of ethanol or chloroform with acetonitrile at room temperature (r.t.) bright yellow solutions of **2a**–**k** were obtained (Scheme 1). After removal of the solvents, these palladium(II) complexes slowly decompose [19]. Spectroscopic data of **2a**–**k** are summarized in Section 4 [20].

Table 1
Selected interatomic distances (Å) and angles (°) for **4n**

Bond lengths			
Pd–N(1)	2.103(3)	Pd–P(2)	2.2501(8)
Pd–N(2)	2.125(3)	C(16)–C(17)	1.459(5)
Pd–P(1)	2.2507(8)	C(18)–C(19)	1.456(4)
Bond angles			
N(1)–Pd–N(2)	87.18(11)	P(1)–Pd–P(2)	91.42(3)
N(1)–Pd–P(1)	90.05(8)	N(2)–Pd–P(2)	90.98(8)

If $(PhCN)_2PdCl_2$ is subjected to a CH_2Cl_2 solution of the diphosphines **1l**–**x**, the colorless, air-stable palladium(II) complexes **3l**–**x** are formed (Scheme 1), which were purified by recrystallization from different solvents. Chloride abstraction to give the dicationic bis(acetonitrile)palladium(II) complexes **4l**–**x** succeeded with two equivalents of $AgBF_4$ in CH_2Cl_2/CH_3CN. In the presence of moist air, acetonitrile is slowly exchanged for water. Whereas **4l**–**x** are soluble in polar or even less polar organic media, **4u**, which is provided with tetradecyl substituents, is also soluble in non-polar media.

2.2. Crystal structure of *4n*

The dicationic diphospalladium(II) complex **4n** crystallizes in the monoclinic space group $P2_1/n$ with four formula units per unit cell [20]. The bond angles P1–Pd–P2 (91.42(3)°) and N1–Pd–N2 (87.2(1)°) differ slightly from an ideal square-planar geometry (see Table 1). Remarkably the six-membered ring, formed by the diphos ligand and the metal atom, is arranged in a chair conformation (Fig. 1). The Pd center and the C2 atom are located 0.463(2) Å below and 0.744(4) Å above the plane that is formed by the atoms P1, P2, C1, and C2. The coordination of acetonitrile to the palladium atom causes longer N–C (N1–C16 = 1.137(4) and N2–C18 = 1.138(4) Å) and C–C distances (C16–C17 = 1.459(5) and C18–C19 = 1.456(4) Å) compared to non-coordinated acetonitrile (N≡C = 1.117(7) and $C–CH_3$ = 1.430(7) Å) [21].

2.3. Copolymerization of ethene with carbon monoxide

The copolymerization of olefins with carbon monoxide is controlled by different factors, which originate from chemical and physical effects. Steric and electronic properties of the catalysts and the substrate molecules, but also the solubility of the starting materials in the corresponding solvent, and their transport over the gas–liquid boundary have to be taken into account. The efficient synthesis of the ligands **1a**–**x** (Scheme 1) offers an easy access to a variety of diphospalladium(II) complexes **2a**–**k** and **4l**–**x** with adjustable steric and electronic properties. Two series of palladium complexes with hydroxyalkyl and alkyl substituents attached to the phosphorus donors were employed in the copolymerization in dichloromethane with small amounts of methanol as activator (**4l**–**u**, Fig. 2), [22] methanol (**2a**–**k**, **4l**–**t**, Fig. 3), and water (**2a**–**k**, Fig. 4) as solvents. In order to eliminate the coordinating carboxylate anions, an excess of HBF_4 was added to the catalyst solutions of **2a**–**k**. In dichloromethane and methanol a polymerization temperature of 60°C proved to be optimal, while in water the highest reaction rates were observed at 80°C. Generally an increased catalytic

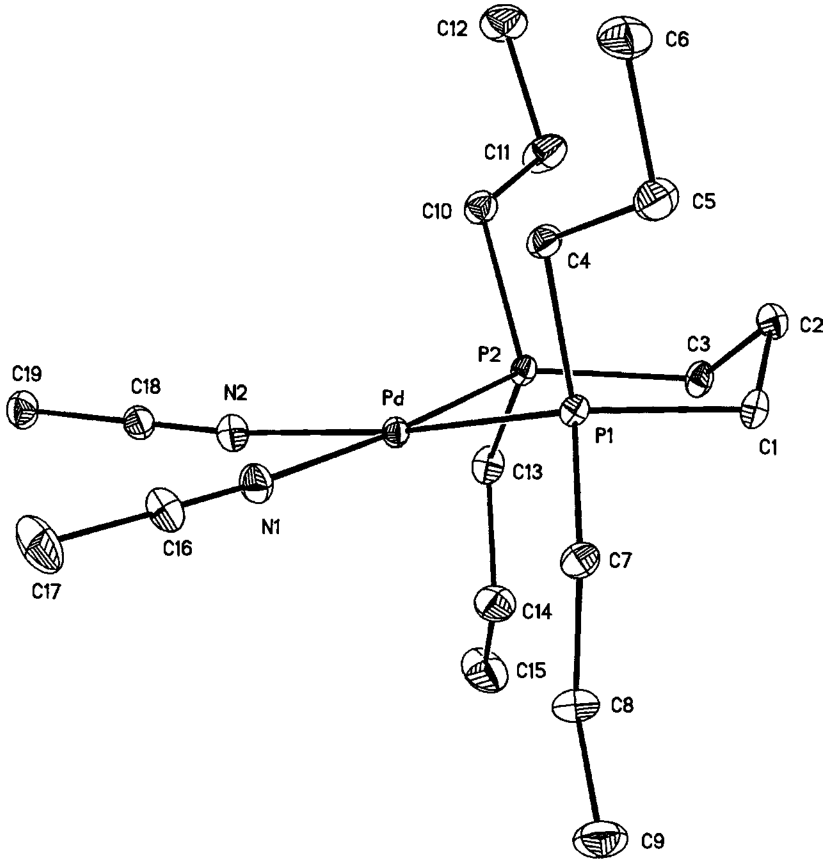

Fig. 1. ORTEP plot of **4n**. Thermal ellipsoids are drawn at the 20% probability level.

performance was established upon replacing the $P(CH_3)_2$ or $P(CH_2OH)_2$ groups in **4l** or **2a** for longer alkyl or hydroxyalkyl chains. In the rhodium catalyzed hydrogenation of olefins a similar effect has been reported [23]. If the catalysis is carried out in dichloromethane the catalytic performance between R = Me (**4l**) and longer alkyl chains does not change significantly. Nevertheless, the well known complex $[(dppp)Pd(NCMe)_2][BF_4]_2$ [**(dppp)Pd**] [5b] is still superior to **4a**–**u** (Fig. 2). However, if polar solvents like methanol (Fig. 3) or water (Fig. 4) are employed shorter alkyl groups induce less catalytic activity. With exception of **2a**, which decomposes rapidly under the selected copolymerization conditions, and **2b** being less active than the corresponding non-functionalized complex **4n**, the two complex series **2a**–**g** and **4l**–**t** show a similar catalytic performance in methanol. In this solvent, the **(dppp)Pd** complex remains the most active catalyst. However, the corresponding water soluble **(dppp-SO$_3$)Pd** complex with four *meta* positioned sulfonate groups exhibited lower catalytic activity (see Table 2) in water. Recently reported results by Sheldon and co-workers could not be reproduced under the applied reaction conditions [15c]. Complex **2g**, bearing long $P((CH_2)_8OH)_2$ groups is insoluble in water. However, catalysts with longer alkyl chains can be applied in this medium when the number of hydroxy functionalities is doubled, as in **2h**–**k**. In addition, the increased polarity and modified steric bulk of **2h**–**k** exert a positive impact on the catalytic activity.

The lower efficiency of the catalysts **2a**–**f** and **2h**–**k** in water mainly reflects the poor solubility of ethene in the aqueous phase and the possibility for water to coordinate to the metal center as a ligand, which was demonstrated recently [24]. Crucial steps in the mechanism of the ethene/CO copolymerization are the easy

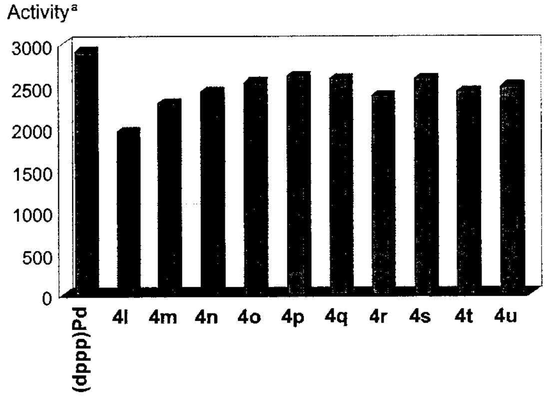

Fig. 2. Catalytic activity in the ethene/CO copolymerization in CH_2Cl_2. ^{a}Activity in (g polymer) × (g Pd × h)$^{-1}$.

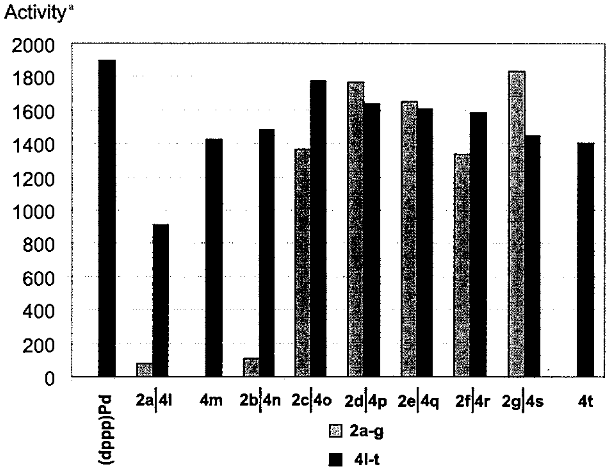

Fig. 3. Catalytic activity in the ethene/CO copolymerization in methanol. ^aActivity in (g polymer) × (g Pd × h)$^{-1}$.

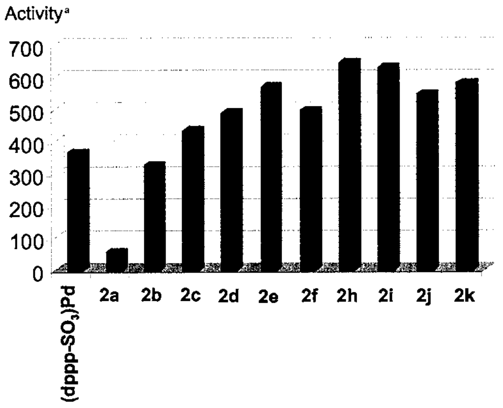

Fig. 4. Catalytic activity in the ethene/CO copolymerization in water. ^aActivity in (g polymer) × (g Pd × h)$^{-1}$.

availability of empty coordination sites and the following π/σ rearrangement of the olefin [1]. The performance of aqueous phase catalysis with the diphospalladium(II) complexes **2a**–**f** and **2h**–**k** is considerably improved by addition of a small amount of methanol, ten equivalents of HBF_4, an anionic surfactant, and a second organic phase (Table 3). An emulsifier (potassium dodecylsulfate) reduces the surface tension of the aqueous phase and accelerates the transport of ethene and CO over the gas–liquid boundary [25]. Optimal results were obtained if the above-mentioned improvements were combined.

2.4. Copolymerization of 1-alkenes with carbon monoxide

Academic and in particular industrial research was mainly focused on the examination of catalysts for the copolymerization of ethene with carbon monoxide, although 1-alkene/CO copolymers have different interesting features. Their physical properties are dependent on the nature of the olefin [8] and the catalysts influence the microstructure of the resulting polymers [13]. With chiral diphospalladium(II) complexes optically active polyketones are accessible, since α-olefins are prochiral [14]. This chapter describes the impact of the chain length of the phosphorus attached alkyl substituents in **4l**–**x** on the 1-alkene/CO copolymerization.

While $[(dppp)Pd(NCMe)_2][BF_4]_2$ [**(dppp)Pd**] is generally superior to **2a**–**k** and **4l**–**x** in the synthesis of ethene/CO copolymers, the latter complexes are successful catalysts if ethene is replaced for 1-alkenes. However, **2a**–**k** and **4l**–**x** are not active if styrene is applied. The copolymerization of carbon monoxide with propene and 1-hexene, respectively (Fig. 5, Table 4), was carried out with complexes **4l**–**x** in dichloromethane in the presence of small amounts of methanol as activator [22]. For both olefins a distinct maximum in the catalytic efficiency in dependence on the length of the alkyl chain was found. At 25°C, the most efficient catalyst in this sequence is **4q**, which is about five times more active than **(dppp)Pd** (Fig. 5, Table 4, runs 1, 7, 25, 29, 35). Unlike the ethene/CO copolymerization the catalytic activity decreases if the bulky diphospalladium(II) complexes **4t**,**u** are applied (Fig. 5, Table 4, runs 9, 10, 38, 39). If the temperature is raised to 60°C not only the catalytic efficiency is clearly improved, also its optimum is shifted to complexes with longer alkyl chains (**4s**,**t**, Fig. 5, runs 23, 24). A further amelioration was achieved by the introduction of branched alkyl groups, although the employment of ^{i}Pr functions (**4v**) results in a deterioration of the catalysis. In particular at 60°C the activity is higher by a factor of 1.5 in the case of complexes **4w**,**x** (Table 4, runs 27, 28). *i*Hex (**4w**) and *neo*Hex (**4x**) substituents represent a compromise between steric shielding and flexibility. Steric and electronic properties of the catalysts also control the molecular weights and the microstructure, (e.g. the regioregularity) of the copolymers (Table 4). In agreement with the catalytic efficiency also the molecular weights are increased on going from shorter to longer alkyl chains (**4l** → **4t**). Ultra high molecular weights of about $M_w = 420\ 000$ g mol^{-1} are obtained with **4s** and **4t** at 25°C. As expected low molecular weights are obtained at 60°C. Generally the molecular weights are lower with an increasing chain length of the 1-alkene (Table 4). However, it should be mentioned that the molecular weights of the 1-hexene and 1-tetradecene/CO copolymers are the highest ever reported ($M_w = 210\ 000$ and $120\ 000$ g mol^{-1}, respectively, Table 4) [8b]. DSC measurements of the polyketones obtained with propene and CO show weak glass transitions of −5 to 10°C and little distinct melting points between 130 and 150°C. In contrast to the elastic material obtained with the **(dppp)Pd** complex [2a], they represent non-elastic thermoplastics. At 60°C brittle products are formed. 1-Hexene and 1-tetradecene/CO

Table 2
Selected catalytic and analytical data of ethene–CO copolymerizations [a]

Run	Compound	Solvent	T_P [b] (°C)	t_P [c] (h)	Activity [d]	Solution viscosity η_{red} (ml g^{-1})	M_w [e] (kg mol^{-1})	D [f]
1	**(dppp)Pd**	CH_2Cl_2 [g]	60	2	2904	n.d.	261.1	2.5
2	**4l**	CH_2Cl_2 [g]	60	2	1945	n.d.	81.9	4.5
3	**4p**	CH_2Cl_2 [g]	60	2	2601	86.64	n.d.	n.d.
5	**4q**	CH_2Cl_2 [g]	60	2	2581	82.34	n.d.	n.d.
6	**4r**	CH_2Cl_2 [g]	60	2	2379	113.96	n.d.	n.d.
7	**4s**	CH_2Cl_2 [g]	60	2	2577	n.d.	119.6	2.5
8	**4u**	CH_2Cl_2 [g]	60	2	2481	119.01	92.8	3.6
9	**(dppp)Pd**	MeOH	60	2	1899	n.d.	1013.4	2.5
10	**4l**	MeOH	60	2	913	n.d.	251.5	1.6
11	**4n**	MeOH	60	2	1479	316.92	n.d.	n.d.
12	**4p**	MeOH	60	2	1770	314.41	n.d.	n.d.
13	**4q**	MeOH	60	2	1608	554.73	n.d.	n.d.
14	**4r**	MeOH	60	2	1585	n.d.	241.2	4.8
15	**2a**	MeOH [h]	60	2	80	n.d.	275.2	4.5
16	**2b**	MeOH [h]	60	2	112	n.d.	171.5	3.2
17	**2c**	MeOH [h]	60	2	1366	n.d.	263.7	3.0
18	**2e**	MeOH [h]	60	2	1648	342.24	246.5	1.4
19	**2f**	MeOH [h]	60	2	1400	n.d.	316.0	1.8
20	**(dppp-SO$_3$)Pd**	H_2O [h]	80	2	365	n.d.	10.1	3.3
21	**2b**	H_2O [h]	80	2	326	n.d.	94.6	3.9
22	**2c**	H_2O [h]	80	2	431	n.d.	89.8	2.9
23	**2d**	H_2O [h]	80	2	487	n.d.	108.8	4.1
24	**2f**	H_2O [h]	80	2	493	n.d.	82.9	3.8
25	**2h**	H_2O [h]	80	2	640	78.79	128.5	2.7
26	**2i**	H_2O [h]	80	2	627	n.d.	159.5	5.1
27	**2j**	H_2O [h]	80	2	545	n.d.	106.2	3.1

[a] The copolymerizations were carried out with 10^{-5} mol of the palladium(II) complexes **2a**–**k** and **4l**–**m** in 30 ml of the corresponding solvent with 30 bar of ethene and carbon monoxide each.

[b] Polymerization temperature.

[c] Polymerization time.

[d] Activity in g polymer × (g Pd × h)$^{-1}$.

[e] Molecular weight determined by GPC.

[f] $D = M_w/M_n$.

[g] 30 ml of CH_2Cl_2 and 2 ml of MeOH.

[h] With 10^{-4} mol of HBF_4.

Table 3
Aqueous phase copolymerization of ethene with CO. Effect of the emulsifier, methanol and toluene on the catalytic activity [a]

Run	Water (ml)	Methanol (ml)	Emulsifier [b] (mg)	Toluene (ml)	Activity [c]	M_w [d] (kg mol^{-1})	D [e]
1	30	0	0	0	567	43.8	2.4
2	30	2	0	0	883	44.0	5.5
3	30	0	300	0	776	40.6	2.1
4	30	0	0	20	1024	51.3	2.4
5	30	0	300	20	1564	56.3	2.6
6	30	2	300	20	1672	46.5	2.2

[a] Copolymerization with **2e** and ten equivalents of HBF_4 at 80°C, 30 bar of ethene and CO each, for 2 h.

[b] Potassium dodecylsulfate.

[c] Activity in g polymer × (g Pd × h)$^{-1}$.

[d] Molecular weight determined by GPC.

[e] $D = M_w/M_n$.

copolymers show no glass transitions, but the material obtained with 1-tetradecene as comonomer melts sharply at 42°C. Inverse gated ^{13}C-NMR spectra were employed to determine the head-to-tail ratio of the 1-alkene/CO building blocks in the polyketones [13]. In the case of propene as a comonomer the head-to-tail ratio is steadily improved in the sequence **4l** to **4t**. The polyketones produced by the complexes **4p** and **4t** are almost perfectly regioregular (Table 4, runs 2–6, 10, 15–20, 24). If 1-hexene and 1-tetradecene are used as comonomers even the catalysts with shorter alkyl chains lead to polyketones with a high regioregularity (Table 4, runs 30–34, 40).

It is remarkable that the water-soluble complexes **2a**–**k**, in particular those which are provided with the described long-chain alkyldiphosphine ligands, are also active in the copolymerization of 1-alkenes with carbon monoxide. At 60°C an unexpected productive biphasic catalytic system consisting of 1-hexene, an aqueous solution of **2d**, ten equivalents of HBF_4, 2 ml of methanol, and potassium dodecyl sulfate, was found (Table 5, run 2). If the anionic surfactant is replaced for neutral (polyethylene glycol) or cationic (benzalkonium tetrafluoroborate) emulsifiers the catalytic efficiency strongly decreases (Table 5, runs 3, 4). The anionic emulsifier affords the best results since it is able to stabilize the positively charged complex at the interface. However, stable emulsions are formed, which prevent the re-use of the aqueous phase. Compared to 1-hexene and 1-decene the catalytic activity in the case of propene as monomer remains low even if toluene is employed as a second phase (see Table 5). This observation is attributed to the poor solubility of propene at 60°C (Table 5, runs 2, 6, 7). Furthermore, under biphasic conditions functionalized olefins like 6-hexenol and 10-undecenol are also successfully copolymerized with CO (Table 5, runs 8, 9).

The remarkable preference of the diphospalladium(II) complexes **2a**–**k** and **4l**–**x** compared to **(dppp)Pd** for α-olefins as comonomers can be proved if these catalysts are employed in terpolymerizations of ethene, 1-alkenes and carbon monoxide.

Semicrystalline polyketones form a new class of polymeric materials with properties in the range of typical engineering thermoplastics such as polyamides, polyesters or polyacetals [1a,26]. Co- and terpolymers of CO, ethene, and 1-alkenes fall within this class. Due to considerable degradation and cross-linking at temperatures above their melting point of 260–270°C, CO/ethene–copolymers exhibit a very narrow window of melt processability [27]. The statistical incorporation of minor amounts of 1-alkenes (e.g. propene, 1-butene, 1-hexene) as termonomers into the CO/ethene copolymer structure leads to easier processable polyketones with lowered crystallinity and melting points. Considerable work has already been done in the area of CO/ethene/1-alkene terpolymers and Shell was the first company to commercialize a CO/ethene/propene terpolymer with a CO/propene content of 5–8 mol% under the trade name Carilon® [1a,8b,14c,26,28].

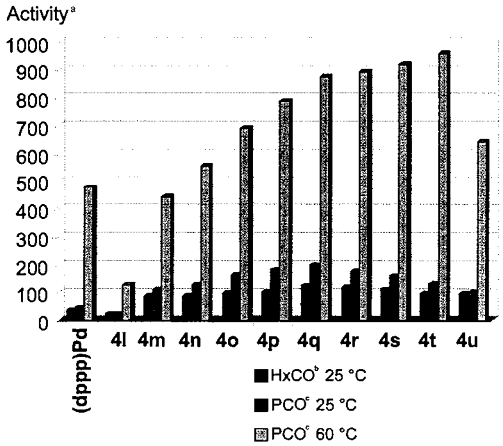

Fig. 5. Catalytic activity in the 1-alkene/CO copolymerization in CH_2Cl_2. ^{a}Activity in (g polymer) × (g Pd × h)$^{-1}$. ^{b}1-Hexene/CO polymerization. ^{c}Propene/CO copolymerization.

As part of these studies on the performance of the water-soluble diphospalladium(II) complexes **2a**–**k** as catalysts in polyketone synthesis, aqueous phase terpolymerization reactions of CO and ethene with propene, 1-hexene, and *N*-vinyl formamide were investigated. In all cases, the polyketones precipitated from the reaction solutions as bright white powders and were completely insoluble in common organic solvents.

In aqueous phase terpolymerization reactions of CO, ethene and 1-hexene, the highest catalyst activities were achieved with the hydroxyhexyl substituted diphospalladium(II) complex **2e**. Running the polymerization at a pressure of 80 bar and a temperature of 90°C with a tenfold excess of *para*-toluenesulfonic acid (relative to the catalyst) and a minor amount of methanol as activators proved optimal in regard of catalytic activity and molecular weights of the terpolymers. Furthermore, by adding an anionic emulsifier such as sodium dodecyl sulfate or a mixture of sodium alkylsulfonates (K30®), we observed a significant increase in catalyst activity and found the terpolymers to be of higher molecular weight and 1-hexene contents (see Table 6). CO/ethene/1-hexene-terpolymers of exceptionally high 1-hexene incorporation resulted from the use of **2f** as catalyst. Generally, the polydispersities M_w/M_n were in the range of 3.7–5.5. However, in some cases (Table 6, runs 6, 8, and 9) the molecular weight distribution (MWD) curves showed bimodal distributions with a small number of polymer chains at very high molecular weights of $> 5 \times 10^5$ g mol^{-1}. This was strongly pronounced in the case of the catalysts **2f** and **2h**. The broad molecular weight distributions seem to indicate that there is more than one type of catalytically active catalyst species or more than one initiation–termination mechanism operating. As was the case for CO/olefin copolymerizations, catalyst activities for **(dppp-SO$_3$)Pd** (both in the form of the acetate complex and the combination of the sulfonated dppp-ligand and $[Pd(CH_3CN)_2((Tosylate)_2]$, **(dppp-SO$_3$)PdTos$_2$**) were significantly lower in CO/ethene/1-alkene terpolymerizations. Furthermore, these catalysts led to terpolymers of lower molecular weight and 1-hexene incorporation when compared to the catalysts stated above.

Table 4
Copolymerization of carbon monoxide with 1-alkenes in dichloromethane

Run	Compound	Olefin [a]	T_{P} [b] (°C)	t_{P} [c] (h)	Activity [d]	TON [e] (cycles)	M_{w} [f] (kg mol^{-1})	D [g]	H–T [h] (%)
1	**(dppp)Pd**	Propene	25	24	45	1642	108.2	3.4	66
2	**4l**	Propene	25	24	22	803	156.2	2.6	75
3	**4m**	Propene	25	24	107	3904	135.0	1.8	95
4	**4n**	Propene	25	24	125	4561	213.6	2.8	98
5	**4o**	Propene	25	24	160	5838	227.0	2.2	~100
6	**4p**	Propene	25	24	181	6604	303.0	2.8	~100
7	**4q**	Propene	25	24	199	7261	235.6	2.3	n.d. [i]
8	**4r**	Propene	25	24	173	6312	321.1	1.9	n.d.
9	**4s**	Propene	25	24	159	5801	414.9	1.5	n.d.
10	**4t**	Propene	25	24	132	4816	418.0	1.9	~100
11	**4u**	Propene	25	24	101	3685	330.4	2.2	n.d.
12	**4v**	Propene	25	24	65	2371	38.7	2.4	n.d.
13	**4w**	Propene	25	24	247	9012	318.4	1.7	n.d.
14	**4x**	Propene	25	24	180	6568	273.9	1.8	n.d.
15	**(dppp)Pd**	Propene	60	4	476	2896	8.5	4.1	64
16	**4l**	Propene	60	4	125	761	22.7	3.7	75
17	**4m**	Propene	60	4	441	2683	24.8	2.3	92
18	**4n**	Propene	60	4	551	3353	23.0	3.8	97
19	**4o**	Propene	60	4	689	4192	23.5	2.7	~100
20	**4p**	Propene	60	4	785	4776	30.4	3.6	~100
21	**4q**	Propene	60	4	872	5306	34.5	3.3	n.d.
22	**4r**	Propene	60	4	890	5415	44.7	3.5	n.d.
23	**4s**	Propene	60	4	916	5573	32.4	3.1	n.d.
24	**4t**	Propene	60	4	959	5835	30.8	3.2	~100
25	**4u**	Propene	60	4	641	3900	26.7	2.9	n.d.
26	**4v**	Propene	60	4	189	1150	5.4	3.5	n.d.
27	**4w**	Propene	60	4	1300	7910	38.0	3.1	n.d.
28	**4x**	Propene	60	4	1421	8646	42.5	3.7	n.d.
29	**(dppp)Pd**	1-Hexene	25	16	32	486	33.6	4.9	75
30	**4l**	1-Hexene	25	16	23	350	85.0	4.0	88
31	**4m**	1-Hexene	25	16	85	1292	124.2	3.7	~100
32	**4n**	1-Hexene	25	16	87	1323	112.2	2.7	~100
33	**4o**	1-Hexene	25	16	96	1459	209.9	2.6	~100
34	**4p**	1-Hexene	25	16	101	1535	155.8	3.5	~100
35	**4q**	1-Hexene	25	16	124	1885	162.8	2.9	n.d.
36	**4r**	1-Hexene	25	16	116	1763	192.8	3.5	n.d.
37	**4s**	1-Hexene	25	16	111	1687	142.5	3.8	n.d.
38	**4t**	1-Hexene	25	16	97	1475	111.8	3.1	n.d.
39	**4u**	1-Hexene	25	16	95	1444	169.4	2.6	n.d.
40	**4q**	1-Tetradecene	24	48	72	1642	118.9	2.9	~100

[a] Propene: 100 ml of CH_2Cl_2, 2 ml of MeOH, saturated with propene at r.t., 51 bar of CO; 1-hexene (1-tetradecene): 70 ml of CH_2Cl_2, 30 ml of 1-hexene (1-tetradecene), 2 ml of MeOH, 60 bar of CO.

[b] Polymerization temperature.

[c] Polymerization time.

[d] Activity in g polymer × (g Pd × h)$^{-1}$.

[e] Turnover number.

[f] Molecular weight determined by GPC.

[g] $D = M_{\mathrm{w}}/M_n$.

[h] H–T: content of head-to-tail connected units.

[i] n.d. = not determined.

Interestingly, performing the polyketone synthesis in the presence of an anionic emulsifier also led to polymer powder samples of increased bulk densities and mean particle sizes. For example, the polyketones obtained in runs 2, 4, and 6 (Table 6) had bulk densities of 0.073, 0.164, and 0.200 g ml^{-1}, respectively, and scanning electron microscopy studies revealed that the polyketone from run 2 was predominantly made up of very small particles (diameters of 10–30 μm) whereas the particle sizes of the materials made accessible in runs 4 and 6 were in the range of 50–120 μm. In conclusion, the 'emulsion process' led to larger and more compact polymer particles which is a very profitable property for further processing.

The addition of the anionic emulsifier leads to a stable emulsion of the 1-alkene in water by finely

Table 5
Aqueous biphasic copolymerization of carbon monoxide with 1-alkenes

Run	Olefin [a]	Surfactant [b]	T_P [c] (°C)	t_P [d] (h)	Activity [e]	TON [f] (cycles)	M_w [g] (kg mol^{-1})	D [h]	H–T [i] (%)
1	1-Hexene	–	60	4	45	170	15.2	72.5	
2	1-Hexene	A	60	4	1746	6636	24.1	21	~100
3	1-Hexene	A	25	4	193	733	3.7	2.5	
4	1-Hexene	N	60	4	53	201	19.0	3.3	
5	1-Hexene	C	60	4	48	182	25.0	3.1	
6	Propene [j]	A	60	4	980	5959	44.0	5.5	
7	1-Decene	A	60	4	794	2012	12.1	3.6	~100
8	5-Hexenol	A	60	8	2340	15564	29.5	4.9	
9	10-Undecenol	A	60	8	1186	5547	14.3	4.4	~100

[a] The copolymerizations were carried out in 30 ml of an aqueous solution of **2f** (10^{-5} mol) with ten equivalents of HBF_4, 2 ml of methanol, 20 ml of the corresponding olefin and 60 bar of CO.

[b] A: anionic surfactant potassium dodecylsulfate; N: neutral surfactant polyethylene glycol-600; C: cationic surfactant benzalkonium tetrafluoroborate.

[c] Polymerization temperature.

[d] Polymerization time.

[e] Activity in g polymer × (g Pd × h)$^{-1}$.

[f] Turnover number.

[g] Molecular weight determined by GPC.

[h] $D = M_w/M_n$.

[i] H–T: content of head-to-tail connected units.

[j] The organic phase consists of toluene that was saturated with propene at r.t.

distributing the latter through micelle formation. Apart from the stabilization of the positively charged catalyst complex, this seems to lead to a higher 1-alkene concentration at the catalytically active site. It may well be, that the polymerization proceeds in a manner comparable to radically induced emulsion polymerizations, in which a water soluble initiator starts the chain growth of the polymer in the aqueous phase. This is then incorporated into the micelles where the polymerization proceeds to the final product.

Under similar reaction conditions, the use of propene and the water-soluble *N*-vinyl formamide as termonomers and complex **2e** as catalyst, led to the corresponding terpolymers with high incorporation of the 1-alkenes. For example, terpolymers with CO/1-alkene contents of 9.7 mol% CO/propene and 6.2 mol% CO/*N*-vinyl formamide were formed at catalyst activities of 1.16 and 0.54 kg (polyketone) g^{-1} (Pd) h^{-1}, respectively.

The melting points of a number of terpolymer samples were measured by DSC. Melting points T_m were detected at 241, 200, and 225°C for samples of CO/ethene/1-hexene, CO/ethene/propene, and CO/ethene/*N*-vinyl formamide terpolymers with 3.3, 9.7, and 6.2 mol% of CO/1-alkene units, respectively. This documents the considerable lowering of the melting point of CO/ethene copolymers by the incorporation of 1-alkenes.

3. Conclusion

The efficient synthesis of the ligands **1a**–**x** (Scheme 1) offers an easy access to a variety of diphospalladium(II) complexes **2a**–**k** and **4l**–**x** with tunable polarity. In particular, the water-soluble hydroxyalkyl functionalized complexes **2a**–**k** represent an alternative to sulfonated aryldiphosphines, which are inconvenient to synthesize. In the copolymerization of olefins with carbon monoxide and **2a**–**k** as catalyst precursors, organic solvents can be replaced for the cheap, non-toxic and non-flammable reaction medium water. A broad spectrum of alkenes from ethene to 10-undecenol is successfully copolymerized with CO and the above-mentioned water-soluble complexes **2a**–**k**. In particular with higher olefins, a remarkable catalytic activity was detected under biphasic polymerization conditions with an anionic surfactant. The high α-olefin chemoselectivity of the alkyldiphospalladium(II) complexes **2a**–**k** and **4l**–**x** compared to **(dppp)Pd** was demonstrated in terpolymerization reactions of α-olefins with ethene and carbon monoxide. This feature facilitates the regulation of the physical properties (e.g. the melting point) of these polyketones. In dependence on the chain-length of the phosphorus attached substituents in **4l**–**x** (i) the regioregularity and (ii) molecular weights of the propene/CO copolymers are controlled and (iii) an optimum in the catalytic activity is formed, (iv) that is shifted to longer alkyl chains when the polymeriza-

Table 6
Results of ethene/CO copolymerizations and ethene/1-hexene/CO terpolymerizations in water

Run	Catalyst [a]	Emulsifier [b] type (g)	Termonomer 1-hexene (g)	Activity [c]	1-Hexene incorp. [d] (mol% 1-hexene/CO)	M_w [e] (kg mol^{-1})	D [f]	Solution viscosity η_{red} (ml g^{-1})
1	**2e**	–	–	1420	–	51.0	4.5	63
2	**2e**	–	20	1230	2.3	50.0	4.4	60
3	**2e**	(A), 0.30	–	1710	–	99.0	4.5	127
4	**2e**	(A), 0.30	20	2320	3.3	91.0	3.7	112
5	**2e**	(D), 0.75	–	1530	–	97.0	4.5	124
6	**2e**	(D), 0.75	20	2560	3.2	96.0	5.5	120
7	**2c**	(D), 0.75	20	1940	3.9	n.d. [f]	n.d.	65
8	**2f**	(D), 0.75	20	1980	5.3	148.0	10.5 (bimodal)	161
9	**2h**	(D), 0.75	20	1500	2.6	163.0	10.0 (bimodal)	174
10	**(dppp-SO_3)Pd**	(D), 0.75	20	320	0.6	45.8	2.8	60
11	**(dppp-SO_3)PdTos$_2$**	–	20	600	0.9	n.d.	n.d.	59
12	**(dppp-SO_3)PdTos$_2$**	(D), 0.75	20	980	0.4	n.d.	n.d.	56

[a] All polymerizations were run in 100 ml of degassed water with 0.02 mmol of the corresponding catalyst in a 300 ml autoclave at 90°C with 40 bar of CO and ethene each for a reaction time of 3 h. In all cases 0.2 mmol of *para*-toluene sulfonic acid and 3 ml of methanol were used as activators.

[b] The emulsifier (A) was sodium dodecylsulfate, emulsifier (D) was K30® (mixture of sodium alkylsulfonates, 40 wt.% in water, product of Bayer AG).

[c] Activity in g polymer $\times$ (g Pd $\times$ h)$^{-1}$.

[d] Determined by NMR spectroscopy.

[e] Determined by gel-permeation chromatography (GPC) against PMMA standard samples.

[f] n.d. = not determined.

tion temperature is raised. The system operates as if a catalytic pocket is formed by the ligand framework, in which the substrate molecules nicely fit.

4. Experimental

4.1. General comments

All experiments were carried out under an atmosphere of argon, if not stated otherwise. Dichloromethane was distilled from calcium hydride, diethyl ether, THF, and toluene from sodium–benzophenone, *n*-hexane from $LiAlH_4$, methanol from magnesium, and acetonitrile from P_4O_{10}. $PdCl_2$ was a gift from Degussa AG. 1-Butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-decene, 1-tetradecene, 4-methyl-1-pentene, and 3,3-dimethyl-1-butene, methylmagnesium chloride (3 M in THF), and ethylmagnesium bromide (1 M in THF) were purchased from Aldrich. The α,ω-hydroxyalkenes used as starting materials are accessible by reacting sodium diethylmalonate with the appropriate alkenyl tosylate followed by hydrolysis and decarboxylation steps [29]. The emulsifiers sodium and potassium dodecyl sulfate, polyethylene glycol-600 and benzalkonium chloride were purchased from Fluka. The emulsifier K30® was purchased from Bayer AG. Benzalkonium tetrafluoroborate was obtained from benzalkonium chloride with $NaBF_4$ in acetone. The diprimary phosphine 1,3-diphosphinopropane, [16] dppp, [30] **dppp-SO$_3$**, [15c] and **1a** [17] were synthesized according to literature methods. Propene, ethene, and carbon monoxide were gifts from BASF Aktiengesellschaft. Elemental analyses were carried out on a Carlo Erba analyzer, model 1106 and Elementar, model Vario EL; Cl analyses were carried out according to Dirschel and Erne [31] and Schöniger [32]. The high resolution ^1H-, $^{13}C\{^1H\}$-, and $^{31}P\{^1H\}$-NMR spectra were recorded on a Bruker DRX 250 spectrometer at 296 K. Frequencies and standards are as follows: $^{13}C\{^1H\}$-NMR 62.90 MHz, $^{31}P\{^1H\}$-NMR 101.25 MHz. Chemical shifts in the ^1H, and $^{13}C\{^1H\}$ spectra were measured relative to partially deuterated solvent peaks and to deuterated solvent peaks, respectively, which are reported relative to TMS. $^{31}P\{^1H\}$ spectra were measured relative to 85% H_3PO_4. The terpolymer microstructures were analyzed by ^1H (250 MHz)- and ^{13}C (62.8 MHz)-NMR spectroscopy on a Bruker instrument DPX 250 in hexafluoroisopropanol/C_6D_6 as solvent with TMS as external standard. The CP/MAS solid-state NMR spectra were recorded on a Bruker DSX 200 and a Bruker ASX 300 multinuclear spectrometer equipped with wide bore magnets (field strengths 4.7 and 7.05 T). Magic angle spinning was applied up to 10 kHz (4 mm ZrO_2 rotors) and 3–3.5 kHz (7 mm ZrO_2 rotors). Frequencies and standards: ^{13}C, 50.288 MHz (4.7 T), 75.432 MHz (7.05 T), respectively (TMS, carbonyl resonance of glycine ($\delta = 176.03$) as the second standard); ^{31}P, 121.49 MHz (85% H_3PO_4, $NH_4H_2PO_4$ ($\delta = 0.8$) as second standard). Chemical shifts are reported in ppm. Mass spectra were acquired on a Finnigan MAT 711A modified by AMD 'Meß- und Datensysteme' (8 kV, 303 K) and reported as mass/charge (*m*/*z*). IR spectra were recorded on a Bruker IFS 48 FTIR spectrometer. DSC measurements were performed on a Mettler-Toledo TA8000 or on a DuPont 2000 instrument (20 K min^{-1}). Glass transitions refer to the onset temperatures of the second heating cycle. Molecular weights were determined by means of gel permeation chromatography (GPC), using a set-up consisting of a Perkin–Elmer Series 10 HPLC pump, a Perkin–Elmer LC 90 UV detector, a PSS SDV linear XL column (eluent $CHCl_3$) with a pore size of 10 μm or a PSS PFG linear XL column (eluent 1,1,1,3,3,3-hexafluoroisopropanol containing 0.05 weight percentage of potassium trifluoroacetate) with a pore size of 7 μm. The molecular weights of the terpolymers were measured on Shodex hexafluoroisopropanol columns. All molecular weights refer to narrow distributed polymethyl methacrylate standards. Reduced solution viscosities η_{red} were measured from 0.5 weight percentage solutions of the polyketones in a mixture of *ortho*-dichlorobenzene and phenol (1:1 mixture) at 25°C in a Ubbelohde capillary viscosimeter (Schott, Typ 53720/II). For scanning electron microscopy studies, powder samples were attached to a copper foil, treated with carbon vapor and sputtered with gold. The samples were then measured on a Hitachi S4000FE instrument at 15 kV with a SE detector. Catalyst activities are given as mean values calculated from the polymer yield (g), the reaction time (h) and the amount of catalyst used (g [Pd]).

4.2. General procedure for the preparation of the diphosphines ***1b–k,n–u,w,x***

In a quartz Schlenk tube 1,3-diphosphinopropane and a 10% excess of the corresponding olefin were magnetically stirred and the mixture was irradiated with the ultraviolet light of a mercury high pressure lamp at 20°C. After 10 h, excess olefin was removed under reduced pressure. Further purification was not necessary. Analytical data of selected diphosphine ligands are presented in Sections 4.3, 4.4 and 4.5. Full data sets for all ligands are summarized in Refs. [20,33].

Caution: The phosphines **1n–p** are pyrophoric in contact with cellulose.

4.3. 1,3-Bis[di(6-hydroxyhexyl)phosphino]propane (***1e***)

1,3-Diphosphinopropane (600 mg, 5.55 mmol) and 6-hexenol (2.45 g, 24.4 mmol) were reacted to give **1e**. Yield: 2.79 g (99%). MS (FD, 30°C): *m*/*z* 509.6 [M^+ +

H]. Anal. Calc. for $C_{27}H_{58}O_4P_2$ (508.27): C, 63.75; H, 11.49. Found: C, 63.67; H, 11.39%. IR (film): ν(OH) 3314 cm^{-1}. $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ −30.6 (s). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 61.6 (s, CH_2OH), 32.0 (s, $\mathit{C}H_2CH_2OH$), 30.7 (d, $^1J(PC) = 10.8$ Hz, C^3), 28.4 ($N = 22.2$ Hz[1] [34], C^2), 26.4 (d, $^2J(PC) = 10.8$ Hz, C^4), 25.3 (d, $^3J(PC) = 12.1$ Hz, C^5), 25.0 (s, $\mathit{C}H_2(CH_2)_2OH$), 21.8 (t, $^2J(PC) = 13.0$ Hz, C^1) (for atom labeling see Scheme 1).

4.4. *1,3-Bis[di(n-heptyl)phosphino]propane* (**1r**)

1,3-Diphosphinopropane (907 mg, 8.40 mmol) and 1-heptene (3.62 g, 36.9 mmol) were reacted to give **1r**. Yield: 4.08 g (97%). MS (EI, 70 eV): *m*/*z* 500.3 [M$^+$]. Anal. Calc. for $C_{31}H_{66}P_2$ (500.31): C, 74.35; H, 13.28. Found: C, 73.99; H, 13.00%. $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ −30.4 (s). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 31.8 (s, CH_2), 31.5 (d, $^1J(PC) = 10.8$ Hz, C^3), 29.2–28.7 (m, $C^2 + CH_2$), 27.2 (d, $^2J(PC) = 11.5$ Hz, C^4), 25.9 (d, $^3J(PC) = 12.8$ Hz, C^5), 22.7–22.3 (m, $C^1 + CH_2$), 14.1 (s, CH_3) (for atom labeling see Scheme 1).

4.5. *1,3-Bis(dichlorophosphino)propane [18]*

To a cooled solution (−30°C) of $H_2P(CH_2)_3PH_2$ (10.56 g, 98 mmol) in 150 ml of dichloromethane trichloromethyl chloroformate (52.53 g, 266 mmol) was added dropwise. The mixture was warmed to 25°C and stirred for 6 h. The solvent and phosgene residues were distilled into a cooled flask (−196°C). The crude, brown product was distilled under reduced pressure (86–88°C, 3 mbar) to give 20.5 g (85%) of $Cl_2P(CH_2)_3PCl_2$. MS (EI, 70 eV): *m*/*z* 245.8 [M$^+$]. ^1H-NMR ($CDCl_3$): δ 2.51–2.37 (4H, m, Cl_2PCH_2), 2.24–2.05 (2H, m, $Cl_2PCH_2\mathit{CH_2}$). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 191.2 (s). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 43.3–42.4 ($N = 53.9$ Hz[1] [34], $Cl_2P–CH_2$), 17.2 (t, $^2J(PC) = 14.1$ Hz, $Cl_2PCH_2\mathit{C}H_2$) (for atom labeling see Scheme 1).

Caution: The evolving gases CO and HCl should be bubbled through a trap containing sodium hydroxide solution and then released into the hood by means of a waste-gas line. Trichloromethyl chloroformate is extremely toxic and corrosive, a gas mask should be used for safety. All contaminated glassware has to be washed with an aqueous NaOH solution.

4.6. *General procedure for the preparation of the phosphine ligands* ***1l,m,v***

Stirred solutions of $Cl_2P(CH_2)_3PCl_2$ and the corresponding Grignard reagent in each 50 ml of THF were reacted for 3 h at r.t. The mixture was hydrolyzed with 100 ml of a saturated solution of NH_4Cl in water. The aqueous layer was extracted with diethyl ether (3 × 30 ml). Subsequently the organic phase was dried with anhydrous Na_2SO_4 and the solvent was removed in vacuo. Finally the crude product was distilled under reduced pressure. Analytical data of a selected diphosphine ligand are presented in Section 4.7. Full data sets for all ligands are summarized in Ref. [20].

4.7. *1,3-Bis(dimethylphosphino)propane* (**1l**) *[35]*

1,3-Bis(dichlorophosphino)propane (7.52 g, 30.6 mmol) and CH_3MgCl (50 ml of a 3 M solution in THF, 150 mmol) were reacted to give **1l**. Yield: 4.57 g (91%), b.p. 79–81°C (13 mbar). MS (EI, 70 eV): *m*/*z* 164.0 [M$^+$]. $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ −51.3 (s). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 33.7 ($N = 20.6$ Hz[1] [34], C^2), 22.0 (t, $^2J(PC) = 13.8$ Hz, C^1), 13.9 (d, $^1J(PC) = 12.8$ Hz, CH_3) (for atom labeling see Scheme 1).

4.8. *General procedure for the preparation of the diacetatodiphosphinepalladium(II) complexes* ***2a–k***

To a stirred solution of palladium(II) acetate in 150 ml of acetonitrile a solution of **1a**–**k** in 150 ml of ethanol was added at 25°C. Subsequently the solvents were removed under reduced pressure. Finally the diphospalladium(II) complexes **2a**–**k** were precipitated from ethanol with *n*-hexane and dried in vacuo. Analytical data of a selected complex are presented in Section 4.9. Full data sets for all complexes are summarized in Ref. [33].

4.9. *Diacetato{1,3-bis[di(7-hydroxyheptyl)phosphino]-propane}palladium(II)* (***2f***)

1f (400 mg, 0.709 mmol) was reacted with palladium(II) acetate (159 mg, 0.709 mmol) to give **2f**. Yield: 475 mg (85%). MS (FAB, 50°C): *m*/*z* 729.6 [M$^+$ − OAc]. Anal. Calc. for $C_{35}H_{72}O_8P_2Pd$ (788.83): C, 53.26; H, 9.19. Found: C, 53.50; H, 9.30%. $^{31}P\{^1H\}$-NMR (CD_3OD): δ 19.6 (s). $^{13}C\{^1H\}$-NMR (CD_3OD): δ 178.8 (s, $CH_3\mathit{C}O_2$), 62.9 (s, CH_2OH), 33.7 (s, $\mathit{C}H_2CH_2OH$), 32.4 ($N = 15.5$ Hz[1] [34], C^3), 30.2 (s, CH_2), 27.0–26.8 (m, $C^2 + 2\ CH_2$), 26.0 (s, CH_2), 23.7 (s, $\mathit{C}H_3CO_2$) (for atom labeling see Scheme 1). IR (KBr): ν(OH) 3446, $\nu_{as}(CH_3COO^-)$ 1586, $\nu_s(CH_3COO^-)$ 1406, ν(C–OH) 1069 cm^{-1}.

4.10. *General procedure for the preparation of the dichlorodiphosphinepalladium(II) complexes* ***3l–x***

Stirred solutions of the corresponding phosphine **1l**–**x** and $(PhCN)_2PdCl_2$ in each 20 ml of dichloromethane were reacted for 2 h at r.t. Subsequently the solvent was removed in vacuo. Finally the complexes **2l**–**x** were

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[1] AXX′ pattern, $N = |^1J(PC) + {}^3J(PC)|$

washed with cold *n*-hexane (−30°C, 3 × 20 ml) and recrystallized from DMSO/acetonitrile (**3l**), acetonitrile/toluene (**3m**), toluene (**3n**,**x**), toluene/*n*-hexane (**3m**–**t**,**v**,**w**) or *n*-hexane (**3u**) to give colorless, crystalline complexes. Analytical data of a selected complex are presented in Section 4.11. Full data sets for all complexes are summarized in Ref. [20].

*4.11. Dichloro{1,3-bis[di(n-heptyl)phosphino]propane}-palladium(II) (**3r**)*

1r (560 mg, 1.120 mmol) was reacted with $(PhCN)_2PdCl_2$ (391 mg, 0.993 mmol) to give **3r**. Yield: 578 mg (86%), m.p. 158°C. MS (FD, 30°C): *m*/*z* 642.6 [$M^+ - Cl$]. Anal. Calc. for $C_{31}H_{66}Cl_2P_2Pd$ (677.69): C, 54.91; H, 9.81; Cl, 10.46; Pd, 15.71. Found: C, 54.62; H, 9.74; Cl, 10.32; Pd, 16.03%. $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 19.2 (s). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 31.6 (s, CH_2), 31.1 (N = 14.9 Hz[1] [34], C^3), 28.9 (s, CH_2), 28.2 (N = 34.9 Hz[1] [34], C^2), 25.4 (s, C^5), 22.5 (s, CH_2), 21.3–20.7 (m, $C^1 + C^4$), 14.0 (s, CH_3) (for atom labeling see Scheme 1).

*4.12. General procedure for the preparation of the dicationic bis(acetonitrile)-diphospalladium(II) complexes **4l**–**x***

To a solution of the corresponding dichloropalladium(II) complex **3l**–**x** in 10 ml of CH_2Cl_2 a solution of $AgBF_4$ in 10 ml of CH_3CN was added and the mixture was stirred for 1 h at r.t. Subsequently the suspension was centrifuged, decanted and the solvent was removed in vacuo. The crude product was dissolved in CH_2Cl_2 and centrifuged again to remove traces of AgCl. Finally the solvent was removed under reduced pressure to give the dicationic complexes **4l**–**x**. Analytical data of a selected complex are presented in Section 4.13. Full data sets for all complexes are summarized in Ref. [20].

*4.13. Bis(acetonitrile){1,3-bis[di(n-heptyl)phosphino]-propane}palladium(II) bis(tetrafluoroborate) (**4r**)*

3r (370 mg, 0.546 mmol) was reacted with $AgBF_4$ (211 mg, 1.09 mmol) to give **4r**. Yield: 457 mg (97%), m.p. 124°C (dec.). MS (FAB, 50°C): *m*/*z* 776.5 [$M^+ - BF_4$]. Anal. Calc. for $C_{35}H_{72}B_2F_8N_2P_2Pd$ (862.43): C, 48.72; H, 8.41; N, 3.25; Pd, 12.35. Found: C, 48.40; H, 8.63; N, 2.96; Pd, 12.88%. IR (KBr): ν(CN) 2323, 2294, $\nu(BF_4)$ 1063 cm^{-1}. $^{31}P\{^1H\}$-NMR (CD_3CN): δ 24.9 (s). $^{13}C\{^1H\}$-NMR (CD_3CN): δ 32.4 (s, CH_2), 31.7 (N = 29.2 Hz[1] [34], C^3), 29.6 (s, CH_2), 27.3 (N = 40.6 Hz[1] [34], C^2), 25.6 (s, C^4), 23.4 (s, CH_2), 19.5–18.7 (m, $C^1 + C^5$), 14.5 (s, CH_3) (for atom labeling see Scheme 1).

4.14. Copolymerization of ethene with carbon monoxide

A solution of the corresponding diphospalladium(II) complex **2a**–**k** (0.01 mmol, 0.1 mmol of HBF_4, 30 ml of water or methanol), was placed in a magnetically stirred steel autoclave, which was charged with 30 bar of ethene and carbon monoxide each. The complex solutions of **4l**–**x** (30 ml of CH_2Cl_2, 2 ml of methanol) were treated in the same way. The reaction temperature was adjusted by a thermostat. Finally the gases were released automatically after 2 h. The puffy, colorless copolymer was collected by filtration and dried in vacuo. A reproducibility of about 10% was found.

4.15. Copolymerization of α-olefins with carbon monoxide

The copolymerization of propene, 1-hexene and 1-tetradecene with carbon monoxide was carried out in a 250 ml mechanically stirred steel autoclave with electrical heating, and air cooling. The evacuated autoclave was charged with a solution of the corresponding dicationic palladium(II) complex **4m**–**x** (0.01 mmol) in CH_2Cl_2 (70 ml), 1-hexene or 1-tetradecen (30 ml) and CH_3OH (2 ml) as activator and 60 bar of carbon monoxide. In the case of propene the catalyst solution (100 ml of CH_2Cl_2) was saturated with the olefin (20°C, 20 min) and pressurized with 51 bar of carbon monoxide. At the end of the reaction period the gases were released automatically. The 1-alkene/carbon monoxide copolymers were obtained by evaporation of the solvent.

The biphasic experiments were carried out in the same reactor set-up as the ethene/CO copolymerizations. The aqueous catalyst solution of **2a**–**k** (0.01 mmol of **2a**–**k**, 0.1 mmol of HBF_4, 30 ml of water, 0.3 g of the corresponding emulsifier) was reacted with 20 ml of the 1-alkene (1-hexene, 1-decene, 6-hexenol, 10-undecenol) and 60 bar of CO at 60°C. In the case of propene 20 ml of toluene were saturated at 20°C and applied as organic phase. The polyketones were collected by filtration and washed with methanol.

4.16. CO/ethene/1-alkene terpolymerization reactions

Terpolymerization reactions were performed in a 300 ml autoclave, equipped with a mechanical stirrer, by the following procedure: 100 ml of degassed water, 20 g (0.24 mol) of 1-hexene or 35 g (0.49 mol) of *N*-vinyl formamide and the emulsifier (see Table 6) were stirred under N_2 to form a stable emulsion. The emulsion was then transferred to the autoclave, under N_2. A solution of the catalyst complex (0.02 mmol) and cocatalyst *para*-toluene sulfonic acid (0.2 mmol) in 3 ml of methanol was added, the autoclave sealed and purged with N_2 and CO/ethene gas (1:1 mixture) twice. Then the pressure and temperature were set to 80 bar and 90°C using CO/ethene gas (1:1 mixture). After 3 h at constant temperature and pressure, the autoclave was vented and the reaction mixture cooled to r.t. The polymer suspension was filtered, washed with methanol and acetone and dried overnight at 80°C in vacuum.

In case of CO/ethene/propene terpolymerization reactions a 3.5 l autoclave equipped with a mechanical stirrer and a catalyst injection port, was evacuated and filled with N_2 in two cycles. Then 1000 ml of degassed water (containing 15 g of K30®, sodium alkylsulfonates, 40 weight percentage in water) and 150 g (3.57 mol) of propene were introduced to the autoclave. The mixture was purged with CO/ethene gas (1:1 mixture). Then the pressure and temperature were set to 80 bar and 90°C using CO/ethene gas (1:1 mixture). Under these conditions, the reaction was started by the injection of the catalyst solution (0.02 mmol **2e** and 0.175 mmol *para*-toluene sulfonic acid in a mixture of 10 ml of water and 3 ml of methanol). After 5 h at constant temperature and pressure, the autoclave was vented and the reaction mixture was cooled to r.t. The polymer suspension was filtered, washed with methanol and acetone and dried overnight at 80°C in vacuum.

Table 7
Crystal data and refinement details for complex **4n**

	4n
Formula	$C_{19}H_{40}B_2F_8N_2P_2Pd$
Formula weight	638.49
Color	Colorless
Crystal dimensions (mm)	0.3 × 0.2 × 0.1
Crystal system	Monoclinic
Space group	$P2_1/n$ (no. 14)
a (Å)	11.318(2)
b (Å)	12.402(7)
c (Å)	21.066(3)
β (°)	103.710(13)
V (Å^3)	2872.6(17)
Z	4
D_{calc} (g cm^{-3})	1.476
T (°C)	−100
F(000) (e)	1304
μ(Mo–K$_\alpha$) (mm^{-1})	0.820
2θ Limits (°)	4.6–54.92
No. of reflections measured	22 833
No. of unique data with $I \geq 2\sigma(I)$	6550
No. of variables	310
S	1.958
R_1 [a]	0.0379
wR_2 [b]	0.0939

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.

[b] $wR_2 = |\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{0.5}$.

4.17. X-ray structural determination of **4n**

Single crystals of **4n** were obtained by slow diffusion of toluene into a concentrated solution of **4n** in acetonitrile. The crystal was mounted on a glass fiber and transferred to a P4 Siemens diffractometer, using graphite-monochromated Mo–K$_\alpha$ radiation. The lattice constants were determined by 18 precisely centered high-angle reflections and refined by least-squares methods. The structure was solved by direct methods [36] and refined by full-matrix least-squares on F^2 using SHELXTL-97 [37]. All non-hydrogen atoms were refined anisotropically (based on F^2). Hydrogen atoms were placed in calculated positions ($d(CH_3) = 0.98$; $d(CH_2) = 0.99$ Å). The final cell parameters and specific data collection parameters for **4n** are summarized in Table 7.

5. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137749. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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