Synthesis of palladium(II) complexes containing a new α-D-xylofuranose-modified diphosphine and their application as catalyst precursors in the co- and terpolymerization of CO–ethene and propene†

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The diphosphine 3,5-dideoxy-1,2-*O*-isopropylidene-3,5-bis(di(2-methoxyphenyl)phosphanyl)-α-D-xylofuranose (*o*-MeO-xylophos), which differs from the known 3,5-dideoxy-1,2-*O*-isopropylidene-3,5-bis(diphenylphosphanyl)-α-D-xylofuranose (xylophos) by the presence of 2-methoxy substituents on the P-aryl rings, has been synthesized and characterized. These two ligands have been employed to stabilize the Pd^{II} complexes [$PdCl_2$(*o*-MeO-xylophos)] (**1a**), [$PdCl_2$(xylophos)] (**2a**), [PdClMe(*o*-MeO-xylophos)] (**1b**), [PdClMe(xylophos)] (**2b**), [Pd(OTs)(H_2O)(*o*-MeO-xylophos)](OTs) (**1c**) and [Pd(OTs)(H_2O)(xylophos)](OTs) (**2c**). All complexes have been characterized by multinuclear-NMR spectroscopy. The solid-state structure of **1a** has been determined by a single crystal X-ray analysis. The Pd–aqua complexes **1c** and **2c** have been employed to catalyse the CO–ethene and CO–propene copolymerization as well as the CO–ethene–propene terpolymerization reaction in MeOH. The catalytic activity and the molecular weight of the polyketones have been compared to those of the products obtained with analogous catalysts, [Pd(H_2O)$_2$(*o*-MeO-dppp)](OTs)$_2$ (**3c**) and [Pd(H_2O)(OTs)(dppp)](OTs) (**4c**), bearing the classical 1,3-bis(diphenylphoshino)propane ligand (dppp). Under comparable catalytic conditions, all catalysts produce structurally similar polymeric materials, with **1c** yielding the largest propene incorporation as well as the highest productivity of low-molecular-weight terpolymers.

Introduction

The design of conformationally rigid polyphosphine ligands for the coordination of late transition metals is a subject of much current interest in organometallic chemistry and homogeneous catalysis, where the selectivity and activity can be significantly influenced by the steric and conformational properties of the metal–diphosphine precursor.[1]

Indeed, in the alternating CO–alkene copolymerization, an effective relation between ligand rigidity and catalytic productivity has been often observed, especially for palladium complexes bearing C_2 and C_3-carbon-bridged diphosphines.[2–4] Besides ligand conformation, an important role in determining both productivity and polyketone molecular weight is also provided by the presence of substituents on the P-aryl rings.[5] In particular, the introduction of one *o*-methoxy substituent on each phosphorus aryl ring of the ligand has been found to greatly enhance the productivity as compared to reactions promoted by catalysts with unsubstituted diphosphines.[6] A recent study has shown that electronic effects, related to the ability of the methoxy oxygen atoms to interact with the metal centre, play a major role in driving the catalytic activity.[7] However, the overall effect on the catalytic activity induced by the combination of ligand conformation and the presence of specific aryl substituents is still rather obscure, especially by varying the experimental conditions, as one may readily realize from a perusal of Scheme 1 that shows the molecular structure of some diphosphines together with the productivity (kg(polyketone) (g(Pd) × h)$^{-1}$) of the corresponding Pd^{II} catalysts in the CO–ethene copolymerization.[6] For catalytic systems based on unsubstituted-phenyl diphosphines (Scheme 1a), the activity does increase with chelating ligand rigidity, whereas no well-defined trend can be drawn for the systems based on *o*-methoxy-substituted ligands (Scheme 1b).

Herein, we report the synthesis and characterization of the 2-methoxy-modified, C_3-bridged diphosphine 3,5-dideoxy-1,2-*O*-isopropylidene-3,5-bis(di(2-methoxyphenyl)phosphanyl)-α-D-xylofuranose (*o*-MeO-xylophos, **1**) (Scheme 2). The preparation of the phenyl derivative xylophos (**2**) has been reported elsewhere.[8]

The mono-cationic Pd^{II}–aqua complexes [Pd(OTs)(H_2O)(P–P)]OTs (P–P = *o*-MeO-xylophos, **1c**; P–P = xylophos, **2c**; OTs = *p*-toluenesulfonate) have been synthesized and employed to catalyze the formation of polyketones by CO–ethene or CO–propene copolymerizations as well as by CO–ethene–propene terpolymerization in MeOH. For comparative purposes, the analogous Pd^{II}–aqua complexes [Pd(H_2O)$_2$(*o*-MeO-dppp)](OTs)$_2$ (**3c**, *o*-MeO-dppp = 1,3-bis(di(2-methoxyphenyl)phosphanyl)propane)[6]

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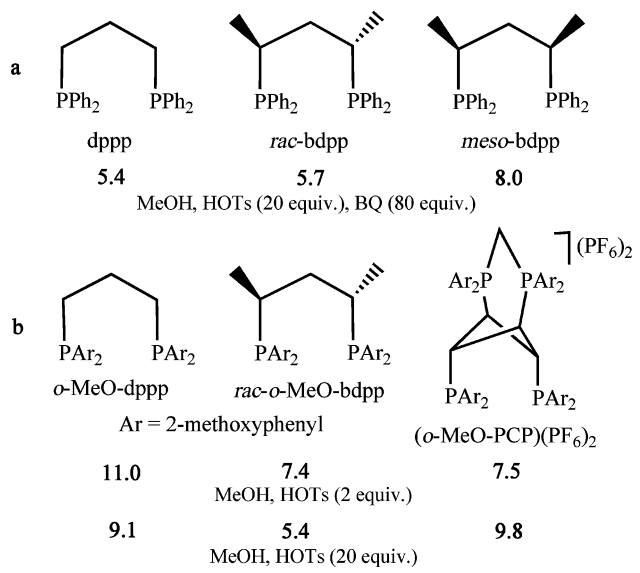
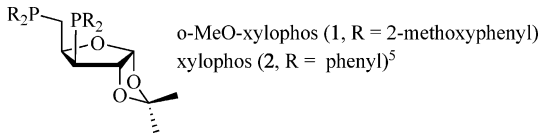


Scheme 1



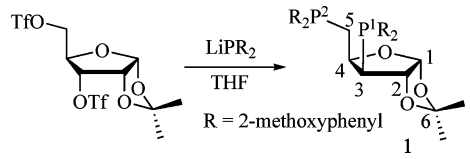
Scheme 2

and [Pd(OTs)(H_2O)(dppp)]OTs (**4c,** dppp = 1,3-bis(diphenylphosphino)propane)[6] were tested under identical experimental conditions as catalyst precursors for the same reactions. As will be shown in this work, where the diphosphines used are amongst the most skeletally rigid ever employed in Pd^{II}-catalysed CO–alkene copolymerization, the presence of *o*-methoxy substituents seems to prevail over any other structural motif in controlling the productivity.

Results and discussion

Synthesis and characterization of the ligand *o*-MeO-xylophos

The new chiral diphosphine ligand *o*-MeO-xylophos (**1**) was synthesized by the reaction of the lithium-salt of bis-(2-methoxyphenyl)phosphine[9] with 1,2-*O*-isopropylidene-3,5-di-*O*-trifluoromethanesulfonyl-α-D-ribofuranose[10] in THF (Scheme 3). The ligand was obtained in 65% yield as a white semi-crystalline compound.

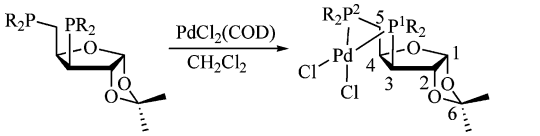


Scheme 3

Ligand **1** was characterized in solution by multinuclear NMR spectroscopy and in the solid state by elemental analysis. In accordance with two non-equivalent phosphorus donor atoms, the $^{31}P\{^1H\}$ NMR spectrum of **1** showed two doublets centred at −50.83 (P^1) and −41.86 ppm (P^2) (Scheme 3), showing a ^4J(P,P) of 15.9 Hz, which is double the value observed for the analogous phenyl-counterpart 3,5-dideoxy-1,2-*O*-isopropylidene-3,5-bis(diphenylphosphanyl)-α-D-xylofuranose (**2**).[8] The methoxy protons gave rise to four ^{1}H-NMR singlets, in the range from 3.62 to 3.83 ppm, which is accounted for by the presence of two different phosphorus donor atoms, each of which bears one axially- and one equatorially-oriented 2-methoxyphenyl unit.

Synthesis and characterization of the palladium complexes with *o*-MeO-xylophos and xylophos

The reaction of [$PdCl_2$(COD)] with either **1** or **2** in dichloromethane yielded the neutral complexes [$PdCl_2$(P–P)] (**1a** and **2a**[11]) as pale yellow air-stable compounds in 74% and 80% yield, respectively (Scheme 4).



Scheme 4

Both complexes were characterized in solution by multinuclear NMR spectroscopy and in the solid state by elemental analysis. The $^{31}P\{^1H\}$ NMR spectra of **1a** and **2a** showed two broad singlets centred at 19.47 and 22.27 ppm and two doublets at 18.20 and 22.8 ppm (^2J(P,P) = 7.4 Hz), respectively. The high-field $^{31}P\{^1H\}$ NMR signal of both complexes (19.47 (**1a**) and 18.20 (**2a**) ppm) has been assigned to the phosphorus atom P^2 (Scheme 4) by means of ^1H–^{31}P correlation spectroscopy. Complex **1a** showed two low-field shifted ^{1}H multiplets, centred at 9.16 and 9.38 ppm, due to palladium–*ortho*-hydrogen atom interactions[6,7,12] which persist also in the solid state, as confirmed by a single crystal X-ray structure analysis. Indeed, crystals of **1a**, suitable for a single crystal X-ray diffraction analysis, were obtained by slow evaporation of a 1 : 1 (v : v) $CHCl_3$–1,4-dioxane solution of **1a** at room temperature. It is worth mentioning that the ORTEP plot shown in Fig. 1 describes the first crystal structure of a transition metal complex bearing a modified α-D-xylofuranosyl moiety. Selected bond distances and angles, as well as experimental diffraction parameters for **1a** are reported in Tables 1 and 3, respectively.

The crystal structure of **1a** exhibits a typically square-planar coordinated palladium atom, which deviates by 0.0257(8) Å in the direction of C(29) from the least-squares coordination plane, defined by the atoms Cl(1), Cl(2), P(1) and P(2), The Pd–P bond lengths of 2.269(1) and 2.246(1) Å (Table 1) are significantly

Table 1 Selected bond length (Å) and angles (°) for **1a**

Pd(1)–Cl(1)	2.349(1)	Pd(1)–P(1)	2.269(1)
Pd(1)–Cl(2)	2.362(1)	Pd(1)–P(2)	2.246(1)
Cl(1)–Pd(1)–Cl(2)	92.81(5)	Cl(1)–Pd(1)–P(1)	174.71(6)
P(1)–Pd(1)–P(2)	91.27(5)	Cl(2)–Pd(1)–P(2)	172.38(5)
Intramolecular distances (Å)			
Pd(1)···O(1)	3.673(4)	Pd(1)···O(4)	3.477(4)
Pd(1)···O(2)	5.207(4)	Pd(1)···H(9)	2.756
Pd(1)···O(3)	5.171(4)	Pd(1)···H(16)	2.894

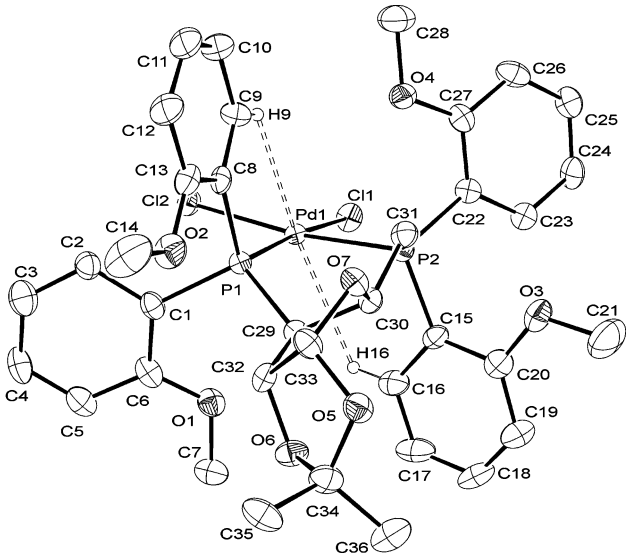


Fig. 1 ORTEP plot of **1a**. The thermal ellipsoids are presented at a 30% probability level and hydrogen atoms are omitted for clarity.

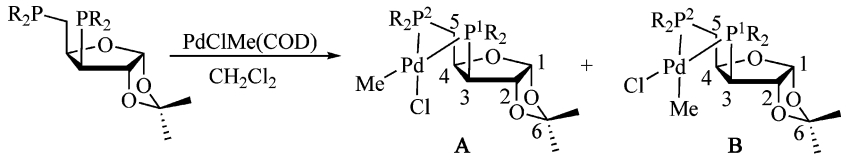
different from each other, due to the different σ-donor properties of the donor atoms, being greater for P(2) than for P(1). As a consequence, the *trans* influence of P(2) is higher than that of P(1) and the Pd(1)–Cl(2) bond length of 2.362(1) Å is significantly longer when compared to the Pd(1)–Cl(1) bond length of 2.349(1) Å. The two bridging carbon atoms C(29) and C(31), which are directly attached to the phosphorus atoms P(1) and P(2), respectively, exhibit an opposite, non-equidistant deviation from the least-squares coordination plane of −0.968(5) and 0.874(6) Å, respectively. This finding suggests a twist conformation of the six-membered ring, which includes the palladium atom. A similar conformation of the six-membered metallaring was predicted for a related Rh–COD complex (COD = cycloocta-1,5-diene) of the type [Rh(COD)(P–P)]BF_4 (P–P = **2**) by means of molecular mechanics calculations.[8] The carbon atoms C(29) and C(30), which show *S* and *R* configurations, respectively, share a six- and a five-membered heterocyclic ring. The latter ring is further connected to a 1,3-dioxolane ring, through the chiral carbon atoms C(32) and C(33), which exhibit an *R* configuration. Both five-membered heterocyclic rings show an envelope conformation. Like related *ortho*-methoxy-modified Pd^{II}–diphosphine complexes,[6,7] the relative spatial orientation of the four 2-methoxyphenyl-groups leads to pair-wise short and long intramolecular palladium–*ortho*-methoxy-oxygen distances, ranging from 3.477(4) to 5.207(4) Å (Table 1).

In order to corroborate the different σ-donor character of the phosphorus atoms of ligands **1** and **2**, the neutral complexes [PdClMe(P–P)] (**1b** and **2b**) were synthesized by reacting [PdClMe(COD)] with a stoichiometric amount of either **1** or **2** (Scheme 5).

Complexes **1b** and **2b** were isolated as white solids in 76 and 83% yield, respectively. The NMR characterization of both compounds in solution showed clearly the presence of geometrical isomers in either case. The ratio between the two isomers A and B (Scheme 5) was found to be 3 : 1 and 5 : 2 for **1b** and **2b**, respectively. The major isomer A exhibited the methyl group coordinated to palladium in a *trans* position with respect to the phosphorus atom P^1, as shown in Scheme 5. Since the methyl group exerts a higher *trans* influence when compared to chloride, the phosphorus atom with the lower σ-donor capacity P^1 is preferentially located *trans* to the methyl group (Scheme 5), which is in line with the results of the single crystal structure analysis (*vide supra*).

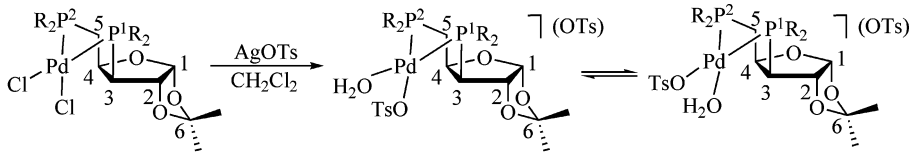
The neutral complexes **1a** and **2a** were transformed into the corresponding mono-cationic aqua complexes [Pd(OTs)(H_2O)(P–P)]OTs (**1c** and **2c**) by the reaction with AgOTs in dichloromethane (Scheme 6).

Complexes **1c** and **2c** were isolated as yellow amorphous compounds in 61 and 64% yield, respectively. Conductivity measurements on both complexes in nitroethane solution showed both compounds to behave as 1 : 1 electrolytes, with one tosylate anion coordinated to palladium.[6,5,13] The fourth coordination site at palladium is apparently occupied by a water molecule which is in fast exchange with the coordinating tosylate anion as shown in Scheme 6. Unlike **1c**, complex **2c** showed a ^{1}H NMR broad singlet at 5.90 ppm, which was assigned to a coordinated water molecule. The $^{31}P\{^1H\}$ NMR spectra in $CDCl_3$ showed a singlet at 25.76 ppm for the former complex, while the latter complex exhibited an AB pattern for the two non-equivalent phosphorus atoms, with two doublets at 21.70 and 21.93 ppm featured by a *J*(P,P) constant of 17.2 Hz. This value is significantly larger than that reported for the corresponding $PdCl_2$-complex **2a**[11] (7.4 Hz), which seems to



R = 2-methoxyphenyl (**1b**), phenyl (**2b**)

Scheme 5



R = 2-methoxyphenyl (**1a**), phenyl (**2a**)

R = 2-methoxyphenyl (**1c**), phenyl (**2c**)

Scheme 6

reflect the weaker *trans* influence of water and tosylate ligands as compared to chloride. As a consequence, the Pd–P bond length for the mono-cationic complex **2c** is shorter than those in **2a** and, thus, it was not surprising to find an increased J(P,P) value for the former complex. A variable temperature $^{31}P\{^{1}H\}$ NMR study of **1c** in $CDCl_3$ showed the coalescence temperature and the slow exchange limit temperature for the water–tosylate exchange process at palladium at −20 and −60 °C, respectively. Indeed, the $^{31}P\{^{1}H\}$ NMR spectrum of the latter complex at −60 °C showed two broad singlets at 25.94 and 26.92 ppm, which were assigned to the atoms P^1 and P^2, while the ^{1}H NMR spectrum at the same temperature contained two unresolved multiplets centred at 9.09 and 9.42 ppm for two *ortho*-hydrogen atoms belonging to the axially oriented 2-methoxyphenyl units. The corresponding ^{1}H NMR spectrum at room temperature exhibited a broad unresolved hump centred at 9.05 ppm for the same hydrogen atoms. Similar low-field shifts of the *ortho*-hydrogen atoms, due to palladium–hydrogen interactions, have already been observed for related neutral and cationic 2-methoxyphenyl-modified palladium diphosphine complexes.[6,7]

Catalytic co-and terpolymerization of CO, ethene and propene

The mono-cationic Pd^{II}–aqua complexes **1c** and **2c** were employed to catalyse the CO–ethene and CO–propene copolymerization reactions as well as the CO–ethene–propene terpolymerization reaction in methanol.[14] It is important to emphasize that, under the catalytic conditions applied, no hydrolysis reaction of the 1,3-dioxolane ring of ligands **1** and **2** was observed. The results of this catalytic study are presented in Table 2.

As a comparison, reactions under identical catalytic conditions were carried out in the presence of the Pd^{II} complexes $[Pd(H_2O)_2(o\text{-MeO-dppp})](OTs)_2$ (**3c**)[6] and $[Pd(H_2O)(OTs)(dppp)]OTs$ (**4c**).[6]

A perusal of Table 2 for the CO–ethene copolymerization reactions shows that, irrespective of the presence or absence of *p*-benzoquinone (BQ), the catalytic productivity of the *ortho*-methoxy modified Pd^{II}–aqua precatalysts follows an opposite trend to that of the analogous phenyl-derivatives (Table 2, entries 7, 8 *vs* 1, 2 and 10, 11 *vs* 4, 5). Indeed, the methoxy-modified dppp precatalyst **3c** was more active than the *o*-MeO-xylophos derivative **1c**, which suggests that the concomitant presence of *ortho*-methoxy substituents on the phenyl rings and of a remarkable ligand rigidity exerts a negative effect on the catalytic productivity. Whether this effect is originated by kinetic or stability factors is hard to say at the present stage. Irrespective of the aryl substituent, the skeletal rigidity reduces the molecular weight of the polyketone products (Table 2, entries 1 and 4 *vs* 7 and 10) that are featured by keto and esters end groups in a 1 : 1 ratio.[14] The lowest average-weight copolymers were actually produced with precatalyst **2c** (Table 2, entry 4). Previous studies have shown that the alternating polyketone molecular weight is controlled by a subtle web of factors.[6,14] As a general trend, the molecular weight decreases by decreasing the basicity of the metal centre (as the termination rate by either methanolysis or protonolysis increases with the electrophilicity of the metal center) as well as by increasing

Table 2 Co- and terpolymerization reactions in methanol employing the cationic palladium–aqua-complexes **1c-4c**

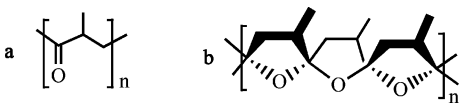
Entry	Pre-catalyst	t/h	*p*-Benzoquinone (equiv.)	Productivity[b]	M_n[c] [M_w/M_n]	Propene (%)	Head-to-tail regio-selectivity[d] (%)
CO–ethene copolymerization[a]							
1[e]	**1c**	1	—	8.4	10.5		
2[e]	**1c**	1	80	14.8			
3[e]	**1c**	3	—	5.6			
4	**2c**	1	—	9.0	3.8		
5	**2c**	1	80	10.0			
6	**2c**	3	—	8.4			
7[e]	**3c**	1	—	13.6	> 35.0		
8[e]	**3c**	1	80	18.1			
9[e]	**3c**	3	—	13.2			
10	**4c**	1	—	3.5	15.0		
11	**4c**	1	80	4.1			
12	**4c**	3	—	2.5			
CO–propene copolymerization[f]							
13	**1c**	3	80	1.8	1.0		48
14	**2c**	3	80	0.7	0.5		57
15	**3c**	3	80	1.1	0.8		57
16	**4c**	3	80	1.2	0.5		66
CO–ethene–propene terpolymerization[f,g]							
17	**1c**	3	80	3.7	3.7 [2.7]	58	
18	**2c**	3	80	1.0	0.8 [1.8]	49	
19	**3c**	3	80	2.5	3.1 [2.3]	53	
20	**4c**	3	80	2.4	1.0 [2.1]	43	

[a] Catalytic conditions: catalytic precursor, 0.0048 mmol; MeOH, 100 mL; $p(CO)/p(C_2H_4)$, 21/21 bar; temperature, 85 °C; stirring rate, 1200 rpm. [b] Productivity expressed as kg(polyketone) (g(Pd) × h)$^{-1}$. [c] M_n expressed as kg mol^{-1}. [d] (h–t) Regioselectivity given in %, based on $^{13}C\{^{1}H\}$ NMR integration. [e] Catalytic precursor, 0.0024 mmol. [f] Catalytic precursor, 0.0048 mmol; MeOH, 100 mL; propene, 30 g and constant CO pressure, 42 bar at 85 °C. [g] $p(C_2H_4)$, 7 bar at 20 °C.

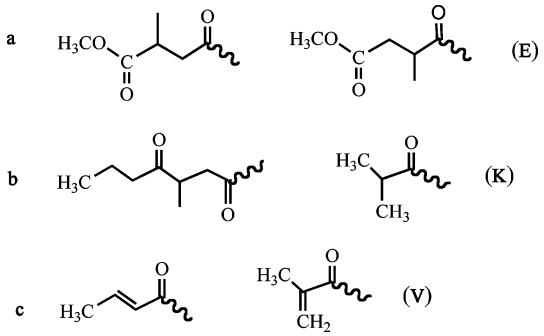
the steric hindrance at the metal centre (as it negatively affects the propagation rate). The effect of the ligand-backbone strain on the basicity of the palladium centre has been estimated by IR spectroscopy analysing the IR ν(CO) of the Rh–dicarbonyl complexes $[Rh(CO)_2(P–P)]PF_6$ (P–P = *o*-MeO-xylophos and *o*-MeO-dppp) in CH_2Cl_2. The observed values of 2094, 2047 cm^{-1} and 2088, 2038 cm^{-1}, respectively, are consistent with a lower σ-donor ability of *o*-MeO-xylophos as compared to its more flexible counterpart *o*-MeO-dppp.

Accordingly, it is possible that the low molecular weights of the polyketones produced with **2c** are due to the synergistic effect of ligand strain and phenyl substituents on the phosphorus donor atoms as the $–PPh_2$ moiety is less basic than the $–P(o\text{-MeO-Ar})_2$ one.[6] Similar effects on the metal nucleophilicity have been reported for other mononuclear Pd complexes containing (P–P) ligands.[4]

In parallel to the CO–ethene copolymerization reactions, CO–propene copolymerizations in MeOH in the presence of BQ were carried out, employing the same precatalysts in the presence of a fixed amount of propene (30 g) and a constant CO feed (Table 2, entries 13–16). ^1H and $^{13}C\{^1H\}$ NMR spectra of the CO–propene products in $CDCl_3$ clearly showed the exclusive formation of poly(1-oxo-2-methyltrimethylene) materials (Scheme 7a) with no trace of poly[*spiro*-2,5-(3-methyltetrahydrofuran)] product (Scheme 7b).[15] Irrespective of the precatalyst, the polyketones contained, ester (E) (Scheme 8a), ketone (K) (Scheme 8b) and vinyl (V) end groups (Scheme 8c), as a consequence of chain-transfer by methanolysis, protonolysis and Pd–β-hydride elimination, respectively.[14,16]



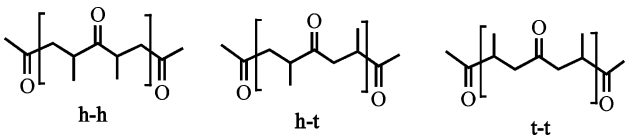
Scheme 7



Scheme 8

Due to the partial overlapping of the ^1H NMR signals of the methyl groups from the ketone-end groups and from the repeating propyl unit, only ^1H NMR-based integral ratios between vinyl (V) and ester (E) end groups can be reported: 1.2 : 3.0 (**1c**), 1.3 : 3.0 (**2c**), 1.0 : 3.0 (**3c**), 1.6 : 3.0 (**4c**). The highest catalytic productivity was observed for **1c** (Table 2, entry 13), while the analogous phenyl derivative **2c** shows the lowest catalytic productivity (Table 2, entry 14).

As for the regioselectivity of the propene enchainment (*i.e.*, 1,2 or 2,1 insertion), all the catalysts gave a lower selectivity than that of dppp (Table 2, entries 13–16). The regioselectivity of the propene insertion into the growing polymer chain was determined by $^{13}C\{^1H\}$ NMR spectroscopy, integrating the ^{13}C CO signals, deriving from tail to tail (t–t), head to tail (h–t) and head to head (h–h) regioisomers. (Scheme 9).[17]



Scheme 9

It is well known, that Pd precatalysts bearing dppp as ligand lead to the only formation of regioirregular copolymers, evidencing thus, that both 1,2- and 2,1-propene insertion into the growing polymer chain occurs with comparable probability.[14,16] Indeed, much higher regioselectivities were obtained with symmetrically substituted C_3-bridged diphosphines bearing either alkyl substituents at the phosphorus donor atoms (Scheme 10a)[16b] or two electronically different phosphorus atoms in combination with a Josiphos-type carbon skeleton (> 99% head-to-tail enchainment) (Scheme 10b).[17]

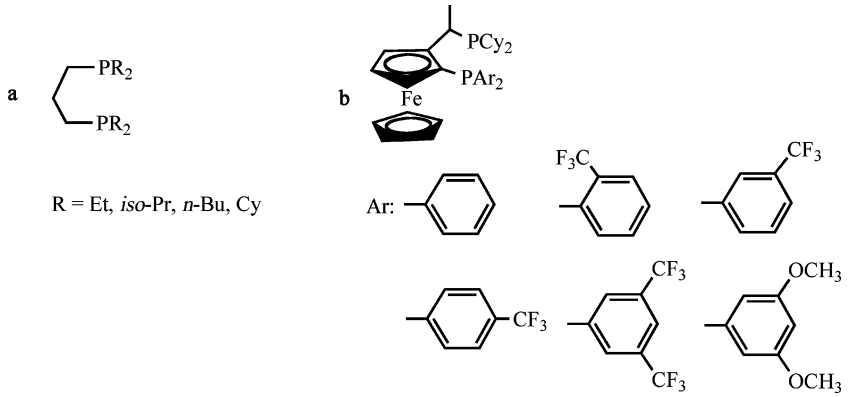
In the present case, neither the substitution of the phenyl groups by the more electron-donating 2-methoxyphenyl group nor the introduction of the chiral α-D-xylofuranose back-bone improved the regioselectivity of the propene enchainment (Table 2).

All four precatalysts (**1c–4c**) were used to catalyse the ter-polymerization reaction of CO–ethene and propene in MeOH, employing a fixed amount of propene (30 g) and ethene (7 bar at 20 °C) (Table 2, entries 17–20). Under these conditions, highly viscous low-molecular weight terpolymers (Table 2, entries 17–20) were obtained.[14,18] The new Pd^{II}–aqua complex **1c** showed the highest propene incorporation and led thus to the highest catalytic productivity within the precatalysts investigated (Table 2, entry 17). The ^1H and $^{13}C\{^1H\}$ NMR spectra of the terpolymers in $CDCl_3$ solutions showed the occurrence of the same type of end-groups and approximately the same vinyl–ester end-group ratios as observed for the CO–propene cooligomers.[18]

Conclusions

The new methoxy modified diphosphine *o*-MeO-xylophos (**1**) and several neutral and cationic Pd^{II} complexes stabilized by **1** or by its phenyl counterpart xylophos (**2**) were synthesized and characterized. Pd^{II}–aqua complexes of the formula $[Pd(OTs)(H_2O)(P–P)]OTs$ (P–P = **1** or **2**) were employed to catalyse the CO–ethene and CO–propene copolymerization as well as the CO–ethene–propene terpolymerization reaction, and their catalytic performance was compared to those of analogous Pd^{II}–aqua complexes bearing the less structurally rigid *o*-MeO-dppp and dppp ligands.

From this comparative catalytic screening, it turned out that: (i) The concomitant presence of *ortho*-methoxy substituents on the P-phenyl rings and of a high conformational rigidity of



Scheme 10

the diphosphine ligand exert a negative effect on the catalytic productivity as compared to the *ortho*-methoxy-dppp-based Pd^{II} precatalyst. (ii) In CO–ethene copolymerization the molecular weight of the polyketones decreases by decreasing the basicity of the chelating diphosphine and increases by decreasing the skeletal rigidity. (iii) Neither the substitution of phenyl with 2-methoxyphenyl nor the introduction of an α-D-xylofuranosyl carbon backbone increases the low regioselectivity of propene insertion as compared to the dppp-based Pd^{II} precatalysts.[16] (iv) The Pd^{II}–aqua complex **1c** with *o*-MeO-xylophos promotes the largest propene incorporation as well as the highest productivity of low-molecular-weight terpolymers. In particular, the productivity with **1c** is comparable to that obtained with the industrial catalytic system comprising an *in situ* generated precatalyst from $Pd(OAc)_2$ and *o*-MeO-dppp and, as solvent, a complex mixture of protic solvents (MeOH–H_2O–HOAc–MeOAc) at a much higher total gas pressure (72 bar).[18]

Experimental

Materials and physical measurements

All reactions and manipulations were carried out under a nitrogen atmosphere by using Schlenk-type techniques. The reagents were used as purchased from Aldrich or Fluka. 1,2-*o*-Isopropylidene-3,5-di-trifluoromethansulfonyl-α-D-ribofuranose,[10] di(2-methoxyphenyl)phosphine,[9] 3,5-dideoxy-1,2-*O*-isopropylidene-3,5-bis-(diphenylphosphanyl)-α-D-xylofuranose, xylophos (**2**),[8] [$PdCl_2$(COD)] (COD = 1,5-cyclooctadiene),[19a] PdClMe(COD),[19b] [$PdCl_2$(xylophos)] (**2a**),[11] [$Pd(H_2O)_2$(*o*-MeO-dppp)]$(OTs)_2$ (**3c**),[6] [Pd(OTs)(H_2O)(dppp)]OTs (**4c**)[6] were prepared according to literature methods. Catalytic reactions were performed using a 320 mL stainless steel autoclave equipped with a mechanical stirrer and a Parr 4842 temperature and pressure controller. All catalytic reactions were carried out at a constant total gas pressure by connecting the autoclave to a gas reservoir. GC/MS analysis of the catalysis solutions were performed on a Shimadzu QP2010S apparatus equipped with a SPB-1 Supelco fused silica capillary column (30 m, 0.25 nm i.d., 0.25 μm film thickness). Deuterated solvents for routine NMR measurements were dried over molecular sieves. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were obtained on either a Bruker Avance II DRX 300 spectrometer (300.13, 75.49, 121.49 MHz, respectively) or a Bruker Avance DRX-400 spectrometer (400.13, 100.62, 161.98 MHz). Chemical shifts are reported in ppm (δ) relative to TMS, referenced to the chemical shifts of residual solvent resonances (^1H and $^{13}C\{^1H\}$ NMR) or 85% H_3PO_4 ($^{31}P\{^1H\}$ NMR). All 2D NMR spectra (*i.e.* ^1H COSY, ^1H–^{13}C and ^1H–^{31}P correlation spectra) were recorded on a Bruker Avance DRX-400 instrument, using deareated non-spinning samples. All NMR spectra were recorded at room temperature, unless stated otherwise. The conductivity measurements of ionic compounds were carried out with an Orion model 990101 conductance cell connected to a model 101 conductivity meter. The conductivity data were obtained at a sample concentration of 10^{-3} M in nitroethane solutions.[20] GPC-analyses were performed in THF (HPLC grade) on a SEC-MALLS system equipped with a WATERS 510 GPC pump, three-serial linear columns (Shodex K80M, Plgel 5 μ Mixed-D Plgel 3 μ Mixed-E), a precolumn (Shodex K800P), two serial detectors, a laser light scattering detector (miniDAWN from Wyatt Technology Corp.) and a refractive index detector (RID-6A from Shimadzu). The data were analysed with ASTRette 1.2 software for Macintosh from Wyatt Technology.

Preparations

3,5-Dideoxy-1,2-*O*-isopropylidene-3,5-bis(di(2-methoxyphenyl)-phosphanyl)-α-D-xylofuranose (1). To a deareated solution of di(2-methoxyphenyl)phosphine (1.14 g, 4.60 mmol) in THF (30 mL), which was cooled to −10 °C by means of an ice–acetone bath, was slowly added butyllithium (4.31 mL (1.6 M), 6.90 mmol). After the complete addition of the latter reagent, the suspension was allowed to stir at room temperature for 1 h, followed by the addition of a solution of 1,2-*O*-isopropylidene-3,5-di-*O*-trifluoromethansulfonyl-α-D-ribofuranose (1.00 g, 2.20 mmol) in THF (20 mL). The reaction mixture was stirred for 3 h at this temperature, followed by the evaporation of the solvent to dryness and redissolving the residue in dichloromethane. The organic phase was washed with water, separated and dried over magnesium sulfate. Then, the solvent was removed completely yielding the compound as a brownish foamy product, which was recrystallized from toluene and ethanol to give the diphosphine as a white semi-crystalline solid. Yield: 65.8% (0.96 g, 1.49 mmol). $C_{36}H_{40}O_7P_2$ (646.27): calc. C 67.90, H 6.19; found C 67.80, H 6.12%. ^1H NMR ($CDCl_3$, 400.13 MHz, ppm): δ 1.17 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 2.67 (dd, $^2J(H^5,H^{5'})$ 13.4 Hz, $^3J(H^5,H^4)$ 6.7 Hz,

1H, H^5), 2.94 (m, 1H, $H^{5'}$), 3.10 (m, 1H, H^3), 3.62 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 4.55 (m, 1H, H^2), 4.59 (m, 1H, H^4), 4.75 (d, $^3J(H^1,H^2)$ 3.6 Hz, 1H, H^1), 6.77–7.57 (m, 16H, Ar–*H*). $^{13}C\{^1H\}$NMR ($CDCl_3$, 100.62 MHz, ppm): δ 26.39 (s, *C*H_3), 26.57 (s, *C*H_3), 26.91 (br s, C^5), 44.65 (d, $^1J(C^3,P^1)$ 19.1 Hz, C^3), 55.43 (s, O*C*H_3), 55.52 (s, O*C*H_3), 77.00 (d, $^2J(C^4,P^1)$ 30.4 Hz, C^4), 84.47 (s, C^2), 104.21 (s, C^1), 109.87 (s, C^6), 110.23–161.93 (Ar–*C*). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.98 MHz, ppm): δ −50.83 (d, $^4J(P^1,P^2)$ 15.9 Hz, P^1), −41.86 (d, $^4J(P^1,P^2)$ 15.9 Hz, P^2).

PdCl$_2$(*o*-MeO-xylophos) (1a). To a deareated solution of ligand **1** (0.22 g, 0.34 mmol) in dichloromethane (10 mL) was added a deareated solution of $PdCl_2$(COD) (0.09 g, 0.32 mmol) in dichloromethane (10 mL) under nitrogen. The solution was allowed to stir at room temperature for 1 h, followed by its concentration to half of the original volume (10 mL). On the addition of diethyl ether (25 mL) the product precipitated as a yellow semi-crystalline compound, which was filtered off, washed with diethyl ether (15 mL) and dried in a stream of nitrogen. Yield: 73.5% (0.21 g, 0.25 mmol). $C_{36}H_{40}Cl_2O_7P_2Pd$ (823.58): calc. C 52.50, H 4.85; found C 52.10, H 4.72%. ^1H NMR ($CDCl_3$, 400.13 MHz, ppm): δ 1.14 (s, 6H, CH_3), 2.77 (ddd, $^2J(H^5,H^{5'})$ 13.4 Hz, $^3J(H^4,H^5)$ 12.2 Hz, $^2J(H^5,P^2)$ 7.2 Hz, 1H, H^5), 3.15 (ddd, $^2J(H^5,H^{5'})$ 13.4 Hz, $^3J(H^4,H^{5'})$ 6.4 Hz, $^2J(H^{5'},P^2)$ 10.4 Hz, 1H, $H^{5'}$), 3.55 (dd, $^3J(H^3,H^4)$ 6.2 Hz, $^2J(H^3,P^1)$ 6.9 Hz 1H, H^3), 3.73 (s, 3H, OCH_3), 3.75 (s, 3H OCH_3), 3.91 (s, 3H, OCH_3), 4.04 (s, 3H, OCH_3), 4.20 (m, 1H, H^4), 4.72 (dd, $^3J(H^1,H^2)$ 3.9 Hz, $^3J(H^2,P^1)$ 7.6 Hz, 1H, H^2), 5.56 (d, $^3J(H^1,H^2)$ 3.9 Hz, 1H, H^1), 6.70–7.80 (m, 26H, Ar-*H*), 9.16 (m, 1H, *o*-Ar-*H*(P^2)), 9.38 (m, 1H, *o*-Ar-*H*(P^1)). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.62 MHz, ppm): δ 24.81 (dd, $^1J(C^5,P^2)$ 33.6 Hz, $^3J(C^5,P^1)$ 19.9 Hz, C^5), 26.34 (s, *C*H_3), 26.54 (s, *C*H_3), 44.39 (dd, $^1J(C^3,P^1)$ 25.0 Hz, $^3J(C^3,P^2)$ 11.9 Hz, C^3), 54.87 (s, O*C*H_3), 55.88 (s, O*C*H_3), 56.60 (s, O*C*H_3), 73.61 (s, C^4), 83.47 (s, C^2), 104.21 (s, C^1), 110.68 (s, C^6), 110.90–161.66 (Ar-*C*). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.98 MHz, ppm): δ 22.27 (br s, P^1), 19.47 (br s, P^2).

PdClMe(*o*-MeO-xylophos) (1b). To a deareated solution of ligand **1** (0.12 g, 0.18 mmol) in dichloromethane (5 mL) was added a deareated solution of PdClMe(COD) (0.05 g, 0.15 mmol) in dichloromethane (5 mL). The clear solution was stirred for 0.5 h at room temperature, followed by concentration to half of the original volume (5 mL). Then diethyl ether (20 mL) was added to yield an off-white solid, which was filtered off, washed with diethyl ether (8 mL) and dried in a stream of nitrogen. Yield: 77.7% (0.11 g, 0.14 mmol). $C_{37}H_{43}ClO_7P_2Pd$ (803.10): calc. C 54.33, H 5.35; found C 54.22, H 5.15%. Compound **1b** was obtained as a 3 : 1 mixture of the geometric isomers A and B as shown in Scheme 5. Integrals of ^1H NMR signals are not reported, due to the partial overlapping of signals, stemming from both isomers. ^1H NMR ($CDCl_3$, 400.13 MHz, ppm): δ 0.28 (dd $^3J(H,P)_{trans}$ 7.1 Hz, $^3J(H,P)_{cis}$ 3.8 Hz, Pd-CH_3(A + B)), 1.14 + 1.15 (s, CH_3), 2.51 (m, H^5(B)), 2.80 (m, H^5(A)), 3.08 (m, $H^{5'}$(B)), 3.18 (m, $H^{5'}$(A)), 3.31 (d, $^3J(H^3,H^4)$ 6.0 Hz, H^3(A)), 3.50 (d, $^3J(H^3,H^4)$ 5.5 Hz, H^3(B)), 3.72 + 3.75 + 3. 98 (s, OCH_3(A + B)), 4.14 (m, H^4(A)), 4.21 (m, H^4(B)), 4.71 (br s, H^2(B)), 4.80 (br s, H^2(A)), 5.50 (s, H^1(A)), 5.53 (s, H^1(B)), 6.68–7.82 (m, Ar-*H*), 8.72 (m, *o*-Ar-*H*), 9.10 (m, *o*-Ar-*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.62 MHz, ppm): δ 9.25 (d, $^2J(C,P^1)$ 105.7 Hz, Pd-*C*H_3(A)), 10.68 (d, $^2J(C,P^2)$ 81.2 Hz, Pd-*C*H_3(B)), 26.09 + 26.19 + 26.25 (s, *C*H_3(A + B)), 26.84 (dd, $^1J(C^5,P^2)$ 33.2 Hz, $^3J(C^5,P^1)$ 20.2 Hz, C^5(A + B), 43.73 (br s, C^3(A)), 46.03 (dd, $^1J(C^3,P^1)$ 21.5 Hz, $^3J(C^3,P^2)$ 11.2 Hz, C^3(B)), 54.52 + 55.67 + 55.73 + 56.21 (s, O*C*H_3(A)), 54.62 + 55.56 + 55.74 + 55.98 (s, O*C*H_3(B)), 74.36 (s, C^4(A + B)), 84.07 (s, C^2(B)), 84.15 (s, C^2(A)), 104.19 (s, C^1(A)), 104.26 (s, C^1(B)), 110.88 + 111.07 (s, C^6(A + B), 110.06–161.62 (m, Ar-*C*(A + B)). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.98 MHz, ppm): δ 1.38 (d, $^2J(P^1,P^2) + {}^4J(P^1,P^2)$ 48.7 Hz, P^2(B)), 5.22 (d, $^2J(P^1,P^2) + {}^4J(P^1,P^2)$ 46.9 Hz, P^1(A)), 26.19 (d, $^2J(P^1,P^2) + {}^4J(P^1,P^2)$ 46.9 Hz, P^2(A)), 31.10 (d, $^2J(P^1,P^2) + {}^4J(P^1,P^2)$ 48.7 Hz P^1(B)).

[Pd(OTs)(H$_2$O)(*o*-MeO-xylophos)]OTs (1c). To a deareated solution of compound **1a** (0.10 g, 0.13 mmol) in dichloromethane (20 mL) was added AgOTs (0.07 g, 0.27 mmol). The suspension was allowed to stir at room temperature, in the absence of daylight, for 2 h, followed by filtration through Celite in order to remove AgCl. The clear solution was concentrated to half of its original volume (10 mL) and then diethyl ether (25 mL) was added to precipitate the product as a yellow solid, which was filtered off, washed with diethyl ether (5 mL) and dried in a stream of nitrogen. Yield: 61.5% (0.09 g, 0.08 mmol). $C_{50}H_{56}O_{14}P_2S_2Pd$ (1112.90): calc. C 53.96, H 5.03; found C 53.71, H 5.06%. ^1H NMR ($CDCl_3$, 400.13 MHz, ppm): δ 1.15 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 2.36 (s, 6H, Ar-CH_3), 2.76 (m, 1H, H^5), 3.18 (m, 1H, $H^{5'}$), 3.59 (m, 1H, H^3), 3.78 (s, 6H, OCH_3), 3.96 (s, 3H, OCH_3), 4.13 (s, 3H, OCH_3), 4.33 (m, 1H, H^4), 4.76 (br s, 1H, H^2), 5.61 (s, 1H, H^1), 6.50–7.90 (m, 22H, Ar-*H*), 8.90–9.20 (br m, 2H, *o*-Ar-*H*). ^1H NMR ($CDCl_3$, 400.13 MHz, −60 °C, ppm): δ 1.11 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 2.12 (s, 6H, Ar-CH_3), 2.80 (m, 1H, H5), 3.28 (m, 1H, $H^{5'}$), 3.41 (m, 1H, H^3), 3.77 (s, 6H, OCH_3), 4.04 (s, 3H, OCH_3), 4.14 (s, 3H, OCH_3), 4.28 (br m, 1H, H^4), 4.80 (s, 1H, H^2), 5.58 (s, 1H, H^1), 6.55–7.90 (m, 22H, Ar-*H*), 9.09 (m, 1H, *o*-Ar-*H*(P^2)), 9.42 (m, 1H, *o*-Ar-*H*(P^1)). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.62 MHz, ppm): δ 21.04 (s, Ar-*C*H_3), 24.08 (dd, $^1J(C^5,P^2)$ 38.9 Hz, ^3J (C^5,P^1) 18.4 Hz, C^5), 26.09 (s, *C*H_3), 26.23 (s, *C*H_3), 43.80 (d, $^1J(C_3,P^1)$ 32.5 Hz, C^3), 55.52 (s, O*C*H_3), 56.08 (s, O*C*H_3), 56.25 (s, O*C*H_3), 56.64 (s, O*C*H_3), 73.31 (s, C^4), 82.51 (s, C^2), 104.35 (s, C^1), 110.81 (s, C^6), 111.20–161.25 (Ar-*C*). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.98 MHz, ppm): δ 25.76 (br s). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.98 MHz, −60 °C, ppm): δ 25.94 (br s, P^2), 26.92 (br s, P^1). Λ_M (nitroethane, 28 °C): 79 Ω^{-1} cm^2 mol^{-1}.

PdClMe(xylophos) (2b). To a deareated solution of ligand **2** (0.16 g, 0.31 mmol) in dichloromethane (5 mL) was added a deareated solution of PdClMe(COD) (0.08 g, 0.31 mmol) in dichloromethane (5 mL). The clear solution was stirred for 0.5 h at room temperature, followed by its concentration to half of the original volume (5 mL) and on the addition of diethyl ether (20 mL) an off-white solid precipitated, which was filtered off, washed with diethyl ether (8 mL) and dried in a stream of nitrogen. Yield: 83.0% (0.17 g, 0.30 mmol). $C_{33}H_{35}ClO_3P_2Pd$ (683.14): calc. C 58.02, H 5.12; found C 58.17, H 5.22%. The product was obtained as a 5 : 2 mixture of the geometric-isomers A and B as shown in Scheme 5. Integrals of ^1H NMR signals are not reported, due to overlapping of signals, stemming from both isomers. ^1H NMR ($CDCl_3$, 400.13 MHz, ppm): δ 0.45 dd, $^2J(H,P^2)$ 8.4 Hz, $^2J(H,P^1)$ 4.4 Hz Pd-CH_3(B)), 0.58 (dd, $^2J(H,P^1)$ 8.0 Hz, $^2J(H,P^2)$ 4.0 Hz Pd-CH_3(A)), 1.16 (s, CH_3(A)), 1.18 (s,

CH_3(B)), 1.27 (s, CH_3(A)), 1.29 (s, CH_3(B)), 2.17 (ddd, $^2J(H^5,H^{5'})$ 13.9 Hz, $^3J(H^4,H^{5'})$ 10.6 Hz, $^2J(H^{5'},P^2)$ 1.8 Hz, $H^{5'}$(B)), 2.65 (ddd, $^2J(H^5,H^{5'})$ 14.6 Hz, $^3J(H^4,H^{5'})$ 10.1 Hz, $^2J(H^{5'},P^2)$ 2.9 Hz, $H^{5'}$(A)), 2.71 (dd, $^3J(H^3,H^4)$ 6.7 Hz, $^3J(H^2,H^3)$ 2.6 Hz, H^3(A)), 2.84 (ddd, $^2J(H^5,H^{5'})$ 13.9 Hz, $^3J(H^4,H^5)$ 6.5 Hz, $^2J(H^5,P^2)$ 3.3 Hz, H^5(B)), 2.98 (ddd, $^2J(H^5,H^{5'})$ 14.6 Hz, $^3J(H^4,H^5)$ 5.8 Hz, $^2J(H^5,P^2)$ 5.6 Hz, H^5(A)), 3.11 (dd, $^2J(H^3,P^1)$ 6.4 Hz, $^3J(H^3,H^4)$ 6.5 Hz, H^3(B)), 4.56 (m, H^4(A + B)), 4.79 (dd, $^3J(H^1,H^2)$ 3.9 Hz, $^3J(H^2,P^1)$ 4.9 Hz, H^2(A)), 4.82 (dd, $^3J(H^1,H^2)$ 4.1 Hz, $^3J(H^2,P^1)$ 7.1 Hz, H^2(B)), 5.47 (d, $^3J(H^1,H^2)$ 4.0 Hz, H^1(A)), 5.67 (d, $^3J(H^1,H^2)$ 4.0 Hz, H^1(B)), 7.40–8.10 (m, Ar-*H*(A + B)). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.62 MHz, ppm): δ 11.86 (d, $^2J(C,P^1)$ 102.4 Hz, Pd-CH_3(A)), 14.09 (d, $^2J(C,P^2)$ 104.0 Hz, Pd-CH_3(B)), 26.03 (s, CH_3(A)) 26.08 (s, CH_3(B)), 26.17 (s, CH_3(B)), 26.20 (s, CH_3(A)), 26.29 (m, C5(B), 29.60 (dd, $^1J(C^5,P^2)$ 30.3 Hz, $^3J(C^5,P^1)$ 20.2 Hz, C^5(A)), 43.97 (dd, $^1J(C^3,P^1)$ 10.6 Hz, $^3J(C^3,P^2)$ 5.4 Hz, C^3(A)), 47.30 (dd, $^1J(C^3,P^1)$ 22.3 Hz, $^3J(C^3,P^2)$ 11.7 Hz, C^3(B)), 74.41 (s, C^4(A)), 74.54 (s, C^4(B)), 82.96 (d, $^2J(C^2,P^1)$ 2.9 Hz, C^2(A)), 83.22 (s, C^2(B)), 103.63 (s, C^1(A)), 103.74 (s, C^1(B)), 111.28 (s, C6(A + B)), 127.02–135.07 (Ar-*C*). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.98 MHz, ppm): δ −4.43 (d, $^2J(P^1,P^2) + {}^4J(P^1,P^2)$ 48.6 Hz, P^2(B)), 1.18 (d, $^2J(P^1,P^2) + {}^4J(P^1,P^2)$ 46.8 Hz, P^1(A)), 25.70 (d, $^2J(P^1,P^2) + {}^4J(P^1,P^2)$ 46.8 Hz, P^2(A)), 31.20 (d, $^2J(P^1,P^2) + {}^4J(P^1,P^2)$ 48.6 Hz, P^1(B)).

[Pd(OTs)(H_2O)(xylophos)]OTs (2c). To a deareated solution of compound **2a** (0.08 g, 0.11 mmol) in dichloromethane (8 mL) was added AgOTs (0.07 g, 0.24 mmol). The yellow suspension was stirred at room temperature, in the absence of day-light, for 2 h, followed by its filtration through Celite in order to remove AgCl. The clear solution was concentrated to half of its original volume (4 mL) and on addition of diethyl ether (20 mL) the product precipitated from the solution as a yellow solid, which was filtered off, washed with diethyl ether (8 mL) and dried in a stream of nitrogen. Yield: 63.6% (0.07 g, 0.07 mmol). $C_{46}H_{48}O_{10}P_2S_2Pd$ (992.90): calc. C 56.64, H 4.83; found C 56.74, H 4.95%. ^1H NMR ($CDCl_3$, 400.13 MHz, ppm): δ 1.25 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 2.33 (s, 6H, Ar-CH_3), 2.73 (m, 2H, $H^5 + H^{5'}$), 3.24 (dd, $^3J(H^3,H^4)$ 7.2 Hz, $^3J(H^3,P^1)$ 8.0 Hz, 1H, H^3), 4.88 (m, 1H, H^4), 5.08 (d, $^3J(H^2,H^1)$ 2.8 Hz, 1H, H^2), 5.90 (br s + d, $^3J(H^1,H^2)$ 2.8 Hz, 3H, $H_2O + H^1$), 6.97–8.02 (m, 28H, Ar-*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.62 MHz, ppm): δ 21.02 (s, Ar-CH_3), 25.44 (dd, $^1J(C^5,P^2)$ 36.6 Hz, $^3J(C^5,P^1)$ 17.9 Hz, C^5), 26.1 (s, CH_3), 26.3 (s, CH_3), 42.30 (dd, $^1J(C^3,P^1)$ 29.8 Hz, $^3J(C^3,P^2)$ 11.0 Hz, C^3), 73.91 (s, C^4), 82.19 (s, C^2), 104.40 (s, C^1), 112.19 (s, C^6), 123.48–141.50 (Ar-*C*). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.98 MHz, ppm): δ 21.70 (d, $^2J(P^1,P^2) + {}^4J(P^1,P^2)$ 17.2 Hz, P^2), 21.93 (d, $^2J(P^1,P^2) + {}^4J(P^1,P^2)$ 17.2 Hz, P1). Λ_M (nitroethane, 28 °C): 65 Ω^{-1} cm^2 mol^{-1}.

X-Ray crystallographic data collection and refinement of the structure of 1a

Crystals, suitable for a single crystal X-ray structure analysis were obtained by slow evaporation of a 1 : 1 (v : v) $CHCl_3$–1,4-dioxane solution of compound **1a** at room temperature. Diffraction intensity data were collected at −103 °C on an Oxford Diffraction CCD diffractometer, operating with graphite-monochromated Cu–K_α radiation ($\lambda = 1.54184$ Å) and using ω-scans. Cell refinement, data reduction, and empirical absorption correction were carried out with the Oxford diffraction software and SADABS, respectively.[21a] All structure determination calculations were performed with the WINGX package,[21b] with SIR-97,[21c] SHELXL-97[21d] and ORTEP-3 programs.[21e] The structure was solved by direct methods and refined by full-matrix F^2 refinement. Final refinements based on F^2 were carried out with anisotropic thermal parameters for all non-hydrogen atoms, which were included using a riding model with isotropic U values 20% larger than those of the adjacent carbon atoms. Crystallographic data for **1a** are reported in Table 3. CCDC reference number for **1a**: 660552.

Table 3 Experimental X-ray diffraction parameters and crystal data for **1a**

Empirical formula	$C_{36}H_{40}Cl_2O_7P_2Pd$
M	823.92
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	11.395(5)
b/Å	17.986(5)
c/Å	20.001(5)
α/°	90.0
β/°	90.0
γ/°	90.0
Unit cell volume/Å^3	4099(2)
D_{calcd}/g cm^{-3}	1.335
Z	4
μ(Mo-Kα)/mm^{-1}	5.936
F(000)	1688
T/°C	−103(2)
λ/Å	1.54184
Absorption correction	SADABS
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameter	5206/0/439
Final R indices	$[I > 2\sigma(I)]$ $R_1 = 0.0415$, $wR_2 = 0.0900$
R indices (all data)	$R_1 = 0.0574$, $wR_2 = 0.0954$
Goodness-of- fit on F^2	0.967
Absolute structure parameter	−0.016(8)
Largest diff. peak and hole/e Å^3	1.045/−0.684

Catalytic co- and terpolymerization reactions

CO–ethene copolymerization reactions in MeOH with 1c–4c as catalyst precursors. In a typical experiment, a MeOH (100 mL) solution containing the catalyst precursor (0.0048 mmol), was introduced by suction into the autoclave (320 mL), previously evacuated using a vacuum pump. When the catalytic reactions were performed in the presence of 1,4-benzoquinone (BQ), this reagent was dissolved in MeOH. The autoclave was charged with a 1 : 1 CO–C_2H_4 mixture to 21 bar at room temperature and then heated to 85 °C, where the pressure was adjusted to 42 bar and the reaction conducted under stirring (1200 rpm) at constant pressure, feeding the autoclave with a 1 : 1 CO–ethene gas-mixture. After the desired reaction time, the autoclave was cooled to room temperature by means of an ice–water bath and the unreacted gases were released. The insoluble copolymer was filtered off, washed with methanol, and dried under vacuum at 50 °C to constant weight.

CO–propene copolymerization in MeOH with 1c–4c as catalyst precursors. In a typical experiment, a MeOH (100 mL) solution containing the catalyst precursor (0.0048 mmol) and BQ (0.0384 mmol) was introduced by suction into the autoclave (320 mL), previously evacuated using a vacuum pump. The

autoclave was cooled to 0 °C, followed by charging it with propene (30 g). Then the autoclave was warmed to 20 °C and charged with CO (7 bar), followed by heating at 85 °C. At this temperature stirring (1200 rpm) was started and the total pressure was adjusted with CO to 42 bar. The reaction was performed at constant pressure upon feeding the autoclave with CO. After a reaction time of 3 h, the autoclave was cooled to room temperature by means of an ice–water bath and the unreacted gases were released. The MeOH solution of the oligomeric material was evaporated at room temperature by means of a vacuum pump to reach constant weight of the cooligomers.

CO–ethene–propene terpolymerization in MeOH with 1c–4c as catalyst precursors. In a typical experiment, a MeOH (100 mL) solution containing the catalyst precursor (0.0048 mmol) and BQ (0.0384 mmol) was introduced by suction into the autoclave (320 mL), previously evacuated using a vacuum pump. The autoclave was cooled to 0 °C, followed by charging it with propene (30 g). Then the autoclave was warmed to 20 °C and charged successively with ethene (7 bar) and CO (7 bar), followed by heating it at 85 °C. At this temperature the total pressure was adjusted with CO to 42 bar and the reaction was conducted under stirring (1200 rpm) and constant CO pressure, feeding the autoclave with CO. After a reaction time of 3 h, the autoclave was cooled to room temperature by means of an ice–water bath and the unreacted gases were released. The viscous MeOH solutions of the terpolymers were evaporated by means of a vacuum pump to reach constant weight of the terpolymers.

Characterization of the CO–ethene, CO–propene copolymers and the CO–ethene–propene terpolymers

The alternating CO–ethene copolymers were analysed by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy, carried out in a 1 : 1 (v : v) solvent mixture of 1,1,1,3,3,3-hexafluoroisopropanol-d_2 and C_6D_6. ^{1}H and $^{13}C\{^{1}H\}$ NMR signals were assigned based on literature reports,[6,14] and the molecular weight determination was based on integration of the corresponding ^{1}H signals.[6]

The alternating CO–propene cooligomers and CO–ethene–propene terpolymers were analysed by ^{1}H and $^{13}C\{^{1}H\}$NMR spectroscopy carried out in $CDCl_3$ as well as by IR spectroscopy. The ratio of the regioisomeric propene incorporation was determined upon integration of the corresponding $^{13}C\{^{1}H\}$ NMR signals, stemming from h–h, h–t and t–t regioisomers,[16] while the amount of propene incorporation in the terpolymers was determined by integration of the corresponding ^{1}H NMR signals. The most significant IR values for the CO–propene cooligomers are: 2966 (w), 2934 (w), 2901 (w), 2879 (w), 1701 (s), 1459 (m), 1388 (m), 1376 (m) and 1023 (m) cm^{-1}. The most significant IR values for the CO–ethene–propene terpolymers are: 2967 (w), 2935 (w), 2904 (w), 1701 (s), 1458 (w), 1394 (m), 1379 (m), 1360 (m) and 1085 (m) cm^{-1}. The molecular weight of the terpolymers was determined by GPC, dissolving them (25 mg) in THF (5 mL, HPLC grade) and using toluene (10 μL, HPLC grade) as standard.

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