A novel linkage-isomeric pair of dinuclear Pd(II) complexes bearing a bis-bidentate tetraphos ligand[†]

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Received 3rd September 2008, Accepted 21st November 2008 First published as an Advance Article on the web 27th January 2009 DOI: 10.1039/b815392b

The tetraphosphane all trans tetrakis-(di(2-methoxyphenyl)phosphanyl)cyclobutane) (o-MeO-dppcb) has been employed to coordinate metal dichlorides (metal = Ni^{II} , Pd^{II} and Pt^{II}), stereoselectively yielding the dinuclear complexes $[Ni_2Cl_4(\mu-(\kappa P^1:\kappa P^2:\kappa P^3:\kappa P^4-o-MeO-dppcb))]$ (3a₆) and $[Pt_3Cl_4(\mu-(\kappa P^1,\kappa P^2;\kappa P^3,\kappa P^4-o-MeO-dppcb))]$ (2a₅), characterized by two six and two five-membered metallacycles, respectively. Conversely, the reaction with PdCl₂ led, under comparable synthetic conditions, to the formation of the linkage-isomeric pair $[Pd_2Cl_4(\mu-(\kappa P^1,\kappa P^2;\kappa P^3,\kappa P^4-o-MeO-dppcb))]$ (1a₅) and $[Pd_2Cl_4(\mu-(\kappa P^1:\kappa P^2:\kappa P^2:\kappa P^3:\kappa P^4-o-MeO-dppcb))]$ (1a₆) in a *ca.* 4 : 1 ratio. The compounds obtained have been characterized in solution by multinuclear NMR spectroscopy and in the solid state by CP-MAS NMR spectroscopy, XRPD and single crystal X-ray diffraction. Compounds $1a_5$ and $1a_6$ have been tested as catalyst precursors for the CO-ethene-propene co-and terpolymerization in water-acetic acid mixtures. Their catalytic performance has been compared to that of $[PdCl_2(o-MeO-dppe)]$ (1b) (o-MeO-dppe = 1,2-(bis(di(2-methoxyphenyl)phosphanyl))ethane) and of $[PdCl_2(o-MeO-dppp)]$ (1c) (o-MeO-dppp = 1,3-bis(di(2-methoxyphenyl)phosphanyl)propane). The most striking result that emerged from the CO–ethene copolymerization study was that **1a**₅ was three times more productive than $1a_6$, outperforming, under identical catalytic conditions, even 1b and **1c**, that are classified amongst the most active catalysts for the CO–ethene copolymerization reaction.

Introduction

The architecture of conformationally rigid polyphosphine ligands for coordination to transition metals is of much current interest in organometallic chemistry and homogeneous catalysis as the overall conformational properties of the corresponding metal– phosphane complexes can significantly influence the catalytic outcome in terms of both activity and selectivity.¹

In the case of CO–ethene copolymerization reactions, a strict relation between ligand rigidity and catalytic performance, especially productivity and average molecular weight of the copolymers, has been observed.² In addition to the ligand skeletal rigidity, also the nature of the phosphane substituents has been found to affect the catalytic activity and selectivity.^{2m,n} For example, the introduction of 2-methoxyphenyl substituents on the phosphorus donor atoms of the ligand has been found to significantly enhance the catalytic productivity of the corresponding Pd^{II} precursors as compared to precursors bearing analogous phenyl-modified diphosphanes, due to a favourable combination of electronic and steric effects.³ A direct interaction between the *o*-methoxy oxygen atoms and

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The reaction conditions for CO–olefin copolymerization can significantly influence the performance of Pd^{II}–diphosphane precursors, as shown by a comparison of the catalytic productivity (kg_(polyketone) g_(Pd)⁻¹ h⁻¹) achieved in MeOH with [Pd^{II}(P-P)]²⁺ compounds, bearing 1,3-bis(di(2-methoxyphenyl)phosphanyl)propane (*o*-MeO-dppp), *rac*-2,4-bis(di(2-methoxyphenyl)phosphanyl)phosphanyl)pentane (*rac-o*-MeO-bdpp) and 6,7-di(di-2-methoxyphenyl)phosphanyl-2,2,4,4-tetra(di-2-methoxyphenyl)-2 λ^4 ,4 λ^4 -diphosphoniumbicyclo-[3.1.1]heptane-bis(PF₆) (*o*-MeO-PCP)-(PF₆)₂ in the presence of different amounts of Brønsted acid (HOTs = *p*-toluenesulfonic acid) (Scheme 1).^{2b,3f}



Scheme 1 Reaction conditions: (a) MeOH, HOTs (2 equiv.); (b) MeOH, HOTs (20 equiv.).

Although MeOH is the solvent of choice for CO-olefine copolymerization reactions, water-acetic acid (AcOH) mixtures

DOI: 10.1039/b815392b

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have been proved to be highly suitable as reaction media for these latter catalytic reactions. This experimental finding may be accounted for by the stabilizing effect of water–AcOH mixtures on Pd–hydride species that are key intermediates in the initiation process of the copolymerization.⁵

Herein, we report the synthesis and characterization of *o*-MeO-dppcb, of a linkage-isomeric pair of palladium complexes of the formula $[Pd_2Cl_4(\mu-(\kappa P^1, \kappa P^2; \kappa P^3, \kappa P^4$ *o*-MeO-dppcb))] (**1a**₅) and $[Pd_2Cl_4(\mu-(\kappa P^1; \kappa P^2; \kappa P^3; \kappa P^4-o-MeO$ dppcb))] (**1a**₆) (*o*-MeO-dppcb = all *trans* tetrakis-(di(2-methoxyphenyl)phosphanyl)cyclobutane), of their analogous Pd–acetate complexes $[Pd_2(OAc)_4(\mu-(\kappa P^1; \kappa P^2; \kappa P^3; \kappa P^4-o-MeO-dppcb))]$ (**5a**₆) and $[Pd_2(OAc)_4(\mu-(\kappa P^1; \kappa P^2; \kappa P^3; \kappa P^4-o-MeO-dppcb))]$ (**5a**₆) and of the related Pt^{II} and Ni^{II} complexes $[Pt_2Cl_4(\mu-(\kappa P^1; \kappa P^2; \kappa P^3; \kappa P^4-o-MeO$ dppcb))] (**2a**₅) and $[Ni_2Cl_4(\mu-(\kappa P^1; \kappa P^2; \kappa P^3; \kappa P^4-o-MeO$ dppcb))] (**3a**₆) (Scheme 2).



Scheme 2

Compounds1a₅ and 1a₆ were tested as catalyst precursors for the alternating CO–ethene–propene co- and terpolymerization reactions in water–AcOH mixtures. The results were compared to those obtained with the mononuclear counterparts [PdCl₂(P-P)] (P-P = 1,2-bis(di(2-methoxyphenyl)phosphanyl)ethane) (*o*-MeOdppe) (1b) and *o*-MeO-dppp (1c) under comparable experimental conditions.

Results and discussion

Synthesis and characterization of o-MeO-dppcb and its complexes

The ligand *o*-MeO-dppcb has been obtained following a synthetic protocol that resembles very much that employed for the synthesis of *cis*,*trans*,*cis*-1,2,3,4-tetrakis(diphenylphosphanyl)cyclobutane.⁶ Scheme 3 shows the basic synthetic steps for the synthesis of *o*-MeO-dppcb.



Ar = 2-methoxyphenyl

Scheme 3

The reaction of the Li-salt of bis(2-methoxyphenyl)phosphane⁷ with *trans*-1,2-dichloroethylene gave *trans*-1,2-(bis(2-methoxyphenyl)phosphanyl)ethylene (*o*-MeO-*trans*-dppen) in low yield (14%). The latter phosphine was reacted with [PtCl₂(η^4 -COD)]

(COD = 1,5-cyclooctadiene) in dichloromethane in a 1 : 1 molar ratio. The obtained Pt intermediate was then irradiated in DMF with a high pressure Hg-vapour UV lamp. Upon reaction of the obtained Pt complex, which was only slightly soluble in DMF, with an excess of NaCN, the free ligand (*i.e. o*-MeO-dppcb) was obtained as white powder in 76.4% yield. The latter ligand is characterized in CD₂Cl₂ at room temperature by a ³¹P{¹H} NMR singlet at -25.8 ppm, while at low temperature (*i.e.* -95 °C) in the same solvent two broad singlets centred at -20.4 and -37.2 ppm have been observed, that have been attributed to the axial and equatorial phosphanyl groups of the tetraphosphine.

The reaction between *o*-MeO-dppcb and $[PdCl_2(\eta^4-COD)]$ in a 1:2 stoichiometric ratio in CH₂Cl₂ at room temperature gave the two dinuclear linkage-isomeric Pd(II) complexes **1a**₅ and **1a**₆ in a *ca.* 4:1 isomeric ratio (Scheme 4). Analogous reactions with $[PtCl_2(\eta^4-COD)]$ and NiCl₂·6H₂O stereoselectively yielded the complexes $[Pt_2Cl_4(\mu-(\kappa P^1,\kappa P^2;\kappa P^3,\kappa P^4-o-MeO-dppcb))]$ (**2a**₅) and $[Ni_2Cl_4(\mu-(\kappa P^1;\kappa P^2;\kappa P^3;\kappa P^4-o-MeO-dppcb))]$ (**3a**₆), respectively (Scheme 4) as a result of the possible coordination modes of the ligand to a metal centre (*i.e.* 1,2 and 1,3 phosphorus coordination to the same metal centre).



The reaction between *o*-MeO-dppcb and $[PdCl_2(\eta^4-COD)]$ was carried out in different solvents (*i.e.* CH₃CN and DMF) with no effect on the isomeric ratio.

Selected bond distances, angles and relative energies of geometry-optimized model complexes (*i.e.* 2-methoxyphenyl groups have been replaced by hydrogen atoms) of the isomeric dinuclear metal chloride compounds and their mononuclear Pd^{II}, Pt^{II} and Ni^{II} counterparts (Fig. 1) are reported in Table 1. A perusal of Table 1 reveals that the dinuclear complexes that contain two sixmembered metallarings (*i.e.* $1a_{6'}$, $2a_{6'}$ and $3a_{6'}$) are lower in energy than the corresponding isomer (*i.e.* $1a_{5'}$, $2a_{5'}$ and $3a_{5'}$), showing a comparable energy gap ($\Delta E(M_5 - M_6)$) within the pairs of isomers (between -23.7 and -25.9 kcal mol⁻¹).

A comparison of the geometrical parameters reported in Table 1 (Cartesian coordinates have been reported as ESI†) showed that the M–P bond distances in the dinuclear metal complexes (*i.e.* $1a_{5'}$, $2a_{5'}$ and $3a_{5'}$) is around 0.03 Å longer as compared to the corresponding isomer, while an analogous comparison with the mononuclear counterparts gave no significant differences (Table 1), indicating that $1a_{5'}$, $2a_{5'}$ and $3a_{5'}$ are characterized by weaker M–P bonds compared to their isomers due to the geometric constraints of the ligand imposed by the cyclobutane ring. On the other hand, the ligand bite angles of the five-membered dinuclear metal complexes are around 4° narrower than in their isomers, while an analogous analysis concerning the mononuclear

 Table 1
 Selected bond distances, angles and relative energies for the optimized metal chloride complexes

	M–Cl/Å	M–P/Å	Cl-M-Cl/°	P-M-P/°	$\frac{\Delta E(M_5 - M_6)}{\text{kcal mol}^{-1}}$
1a _{5'}	2.35	2.30	97.0	91.0	
$1a_{6'}$	2.36	2.27	98.0	96.0	-23.7
1b'	2.35	2.27	97.7	87.5	
1c′	2.36	2.27	97.0	97.1	
2a5'	2.37	2.28	94.0	92.0	
2a _{6'}	2.38	2.25	95.0	96.0	-24.3
2b'	2.38	2.25	94.4	87.8	
2c'	2.38	2.26	93.3	97.4	
3a5'	2.20	2.21	99.0	92.0	
3a _{6'}	2.20	2.18	99.0	96.0	-25.9
3b′	2.20	2.17	100.2	88.3	
3c′	2.21	2.18	97.7	96.8	



Fig. 1 Geometry-optimized model complexes.

complexes (Table 1) showed a difference in the bite angles between the five- and six-membered metallacycles of around $8-10^{\circ}$.

Intrigued by the fact that *o*-MeO-dppcb formed linkage isomers with Pd^{II}, we searched for a synthetic procedure aimed at increasing the yield of **1a**₆ (*i.e.* minor product) (Scheme 4). To this purpose, we exploited (i) the selective coordination of Cr^{III} to *o*-MeO-dppcb (leading to the exclusive formation of six-membered metallarings as occurs with other 3d metals such as Ni^{II} (*vide supra*) and Co^{II})⁸ and (ii) the easy displacement of Cr^{III} from the coordination sphere by Pd^{II}, due to the weaker binding affinity of Cr^{III} to phosphorus donor atoms.⁹

The reaction of $[CrCl_3(THF)_3]$ with *o*-MeO-dppcb in CH₂Cl₂ yielded selectively the pink complex $[Cr_2Cl_6(THF)_2(\mu-(\kappa P^1:\kappa P^2:\kappa P^3:\kappa P^4-o-MeO-dppcb))]$ (**4a**₆) (Scheme 5). The latter complex was isolated and was further reacted with $[PdCl_2(\eta^4-COD)]$ at room temperature to give **1a**₅ and **1a**₆ in a *ca*. 1 : 3 isomeric ratio, which is opposite to the product distribution obtained by the direct reaction of $[PdCl_2(\eta^4-COD)]$ with *o*-MeO-dppcb (Scheme 4).

The further reaction of either $1a_5$ or $1a_6$ with silver acetate (AgOAc) in CH₃CN or THF yielded the CH₂Cl₂-soluble complexes [Pd₂(OAc)₄(μ -(κP^1 , κP^2 : κP^3 , κP^4 -o-MeO-dppcb))] (5a₅) and

 $[Pd_2(OAc)_4(\mu-(\kappa P^1:\kappa P^2:\kappa P^3:\kappa P^4-o-MeO-dppcb))] (5a_6) as yellow powders in 51 and 25% yield, respectively (Scheme 2). The direct reaction of Pd(OAc)_2 with o-MeO-dppcb gave 5a_5 and 5a_6 in an approximately 4 : 1 isomeric ratio as observed for the analogous reaction with [PdCl_2(\eta^4-COD)] (Scheme 4), along with the formation of still unidentified side products.$

The isolated dinuclear metal chloride complexes, possessing two six-membered metallarings (*i.e.* $1a_6$, $3a_6$ and $4a_6$) are soluble in organic solvents such as CH₂Cl₂ and have been straightforwardly characterized by multinuclear NMR spectroscopy and ESI-MS measurements in solution and by elemental analysis in the solid state. Complex 1a₆ was also authenticated by CP-MAS ³¹P NMR spectroscopy and a single crystal X-ray structure analysis. The ³¹P{¹H} NMR spectrum of $1a_6$ acquired in CD₂Cl₂ showed two broad singlets at 17.80 and 36.16 ppm, while $3a_6$ exhibited in the same solvent two doublets at 7.37 and 25.55 ppm with ${}^{2}J(PP)$ of 94.0 Hz indicating two chemically inequivalent phosphorus atoms coordinated to the same metal centre. The CP-MAS ³¹P NMR spectrum of $1a_6$ (Fig. 2) ($\delta = 17.94$ (br s), 38.00 (br s)) along with the single crystal X-ray structure analysis of $1a_6 \cdot 2.8DCE$ (DCE = 1, 2-dichloroethane) unambiguously showed inequivalent phosphorus atoms in the solid state, due to Pd-o-MeO-oxygen interactions (vide infra), persisting also in solution.

Fig. 2 CP-MAS ³¹P NMR spectra of $1a_5$, $2a_5$ and $1a_6$. Spinning sidebands are denoted by asterisks.

Crystals of $1a_6 \cdot 2.8DCE$ suitable for a single crystal X-ray structure analysis have been obtained by a slow evaporation of a DCE solution of $1a_6$ at room temperature. An ORTEP diagram of $1a_6 \cdot 2.8DCE$ is shown in Fig. 3, while selected bond distances and angles as well as crystallographic data are reported in Tables 2 and 4, respectively.

The asymmetric unit of the crystal structure of $1a_6 \cdot 2.8DCE$ contains the metal complex and 2.8 molecules of 1,2-dichloroethane. Two were disordered.

	1a ₆ ·2.8(DCE)	2a ₅
Pt(1)–P(1)		2.2360(15)
Pt(1)-Cl(1)		2.3443(16)
Pd(1)–P(1)	2.258(3)	
Pd(1)–P(2)	2.255(3)	
Pd(1)–Cl(1)	2.379(3)	
Pd(1)-Cl(2)	2.347(3)	
Pd(2)–P(3)	2.254(3)	
Pd(2)–P(4)	2.266(3)	
Pd(2)-Cl(3)	2.347(3)	
Pd(2)-Cl(4)	2.360(3)	
P(1)-Pt(1)-P(1A)		90.91(8)
P(1)-Pt(1)-Cl(1)		89.04(5)
Cl(1)-Pt(1)-Cl(1A)		91.28(8)
P(1)-Pt(1)-Cl(1A)		176.03(5)
P(1)-Pd(1)-P(2)	94.47(11)	
P(1)-Pd(1)-Cl(1)	86.82(11)	
Cl(1) - Pd(1) - Cl(2)	91.94(11)	
P(2)-Pd(1)-Cl(2)	86.80(11)	
P(1)-Pd(1)-Cl(2)	178.64(12)	
P(2)-Pd(1)-Cl(1)	176.27(11)	
P(3)-Pd(2)-P(4)	94.36(10)	
P(3)-Pd(2)-Cl(3)	86.12(10)	
Cl(3) - Pd(2) - Cl(4)	90.86(11)	
P(4) - Pd(2) - Cl(4)	88.69(11)	
P(3)–Pd(2)–Cl(4)	176.19(11)	
P(4) - Pd(2) - Cl(3)	179.24(11)	
Intramolecular distances ((Å)	
$Pt(1) \cdots O(1)$		3.539(5)
$Pt(2) \cdots O(2)$		5.151(4)
$Pd(1) \cdots O(1)$	2.811(8)	
$Pd(2) \cdots O(8)$	2.825(7)	

Symmetry transformation used to generate equivalent atoms: A = y, x, -z.

Fig. 3 ORTEP diagram of $1a_6$ -2.8DCE with 30% probability ellipsoids. Hydrogen atoms, solvent molecules and all 2-methoxyphenyl units showing no interaction with the metal centre have been omitted, instead their *ipso* carbon atoms are presented.

Both palladium atoms of the binuclear complex show a squareplanar coordination environment, built up by two *cis* coordinating chloride atoms and two phosphorus donor atoms attached to the 1,3 positions of the cyclobutane carbon ring, thus forming two six-membered metallarings almost perpendicular to each other with a dihedral angle of $86.34(11)^\circ$. Accordingly, the related mononuclear bis-phosphonium modified complex [PdCl₂(*o*-MeO-

PCP)](PF₆)₂ exhibits a comparable dihedral angle of 86.43(10)°.^{2b} The deviations of the palladium atoms in $1a_6 \cdot 2.8DCE$ from the coordination planes, defined by P(1), P(2), Cl(1) and Cl(2) or P(3), P(4), Cl(3) and Cl(4), are 0.031(1) (Pd(1)) and 0.017(1) Å (Pd(2)), respectively. The cyclobutane carbon ring shows a folding angle of 152.4°. Both ligand bite angles P(1)-Pd(1)-P(2) and P(3)-Pd(2)-Pd(2)P(4) of 94.52(11)° and 94.35(10)°, respectively, are significantly larger than that found for the more flexible mononuclear counterpart 1c of 90.09(4)°, while the Pd–P bond lengths are comparable in either complex: 2.259(3), 2.254(3), 2.254(3) and 2.265(3) Å $(1a_6 \cdot 2.8 \text{DCE})$ vs. 2.250(1) Å (1c).^{3f} A short intramolecular distance between the metal centre and one o-methoxy oxygen atom of each Pd coordination sphere (*i.e.* $Pd(1) \cdots O(1)$ and $Pd(2) \cdots O(8)$ of 2.805(8) Å and 2.825(7) Å, respectively), accounts for the slight asymmetry observed in each coordination sphere of $1a_6$. Analogous interactions have also been found to occur in $3a_6$ (a complete X-ray structure analysis will be reported elsewhere) showing Ni \cdots O distances of 2.620(5) and 2.604(6) Å.

The higher *trans* influence of the acetate ligand as compared to chloride increases the palladium–phosphorus bond length.⁹ As a consequence, the palladium–o-MeO-oxygen interactions that are responsible for the inequivalence of the phosphorus donor atoms in **1a**₆ (*vide infra*) are significantly weakened and hence the Pd acetate complex (**5a**₆) showed a symmetric coordination sphere at palladium, at least on the NMR time scale, indicated by a ³¹P{¹H} NMR singlet at 29.76 ppm.

Due to the insolubility in organic solvents of the dinuclear metal chloride complexes containing two five-membered metallarings (*i.e.* $1a_5$ and $2a_5$) both complexes were characterized in the solid state by CP-MAS ³¹P NMR spectroscopy (Fig. 2), X-ray powder diffraction (XRPD spectra have been reported as ESI†) and elemental analysis, while $2a_5$ was additionally characterized by a single crystal X-ray structure analysis (*vide infra*).

The CP-MAS ³¹P NMR spectra of 1a₅ and 2a₅ (Fig. 2) showed for each complex one singlet centred at 44.60 and 20.29 ppm (${}^{1}J(PtP) = 3717$ Hz), respectively. The chemical shift of the latter compound resembles very much that obtained for the related mononuclear Pt^{II} complex $[PtCl_2(P-P)]$ (P-P = all *trans*-1,2-(bis(diphenylphosphanyl))-3,4diphenylcyclobutane)¹⁰ (δ 26.80 ppm, ¹J(PtP) = 3727 Hz), that is also characterized by a strained five-membered metallaring. A comparison of the ${}^{31}P{}^{1}H$ NMR chemical shift of 5a₅ (δ 35.99 ppm) with that of the flexible mononuclear complex $[Pd(OAc)_2(o-MeO-dppe)]$ (δ 61.94 ppm) clearly indicates that the five-membered ring contribution to the ³¹P chemical shift is low in strained five-membered metallarings. This may be due to hampered electron delocalization via $p\pi$ - $p\pi$ conjugation within the five-membered metallaring as previously suggested to explain, in conjunction with conformational and steric effects, the strong low-field ³¹P NMR chemical shifts observed in transition metalphosphorus chelate complexes.11

The XRPD patterns of $1a_5$ and $2a_5$ confirm that these complexes are isostructural and exhibit a comparable stereochemistry at the metal centre.

Crystals, suitable for a single crystal X-ray structure analysis of $2a_5$ were obtained by controlled diffusion of CH_2Cl_2 solutions of [PtCl₂(η^4 -COD)] and of *o*-MeO-dppcb into each other at room temperature. A selected ORTEP diagram of $2a_5$ is shown in Fig. 4, while selected bond lengths and angles as

Fig. 4 ORTEP diagram of **2a**₅ with 30% probability ellipsoids. Hydrogen atoms as well as all symmetry equivalent 2-methoxyphenyl units are omitted for clarity, instead only their *ipso* carbon atoms are presented. Symmetry transformations used to generate equivalent atoms: y, x, -z; 1 - x, 1 - y, z; 1 - y, 1 - x, -z. The given labelling pertains to the atoms without symmetry transformation (*i.e.* x, y, z).

well as the crystallographic data are reported in Tables 2 and 4, respectively.

The crystal structure of $2a_5$ exhibits in the asymmetric unit only a quarter of the entire molecule (*i.e.* labelled part of Fig. 4), indicating the equivalence of both Pt^{II} coordination spheres, which comprise two *cis*-coordinating chloride ions and two vicinal phosphorus donor atoms of *o*-MeO-dppcb, thus forming two five-membered metallarings sharing a folded (*i.e.* folding angle of 138.7 °) cyclobutane carbon ring. The metal centre exhibits a square-planar coordination geometry, deviating from the coordination plane, defined by the atoms P(1), Cl(1) and their symmetry-equivalent counterparts P(1A) and Cl(1A), by 0.063(1) Å. The ligand bite angle P(1)–Pt(1)–P(1A) of 90.91(8)° is comparable to that observed for the related mononuclear Pt^{II} complex [PtCl₂(P-P)] (P-P = all *trans*-1,2-(bis(diphenylphosphanyl))-3,4-diphenylcyclobutane), 90.15(3)°,¹⁰ but significantly larger than that in complexes bearing the dppe ligand (1,2-bis(diphenylphosphanyl)ethane) (*i.e. ca.* 85°).¹² The rigid twist conformation of the five-membered metallarings in **2a**₅ is clearly evidenced by the symmetry-related deviation of the cyclobutane carbon atoms of 0.447 Å from the least-squares plane defined by Pt(1), P(1), P(1A), Cl(1) and Cl(1A). Unlike **1a**₆, **2a**₅ shows no metal–*o*-methoxy-oxygen interactions (Table 2).

Catalytic co-and terpolymerization of CO, ethene and propene

Complexes $1a_5$ and $1a_6$ were employed to catalyse the CO–ethene and CO–propene copolymerization as well as the CO–ethene–propene terpolymerization reaction in water–AcOH solvent mixtures.^{37,13} For comparative purposes some catalytic reactions were carried out with 1b and 1c as catalyst precursors under identical experimental conditions. The results of the catalytic study are presented in Table 3.

The results obtained with each catalyst precursor are reported for the maximum of productivity observed (Table 3) which was actually achieved with $1a_5$ and $1a_6$ in a 65 mol% water–HOAc mixture with 1b and 1c in a 75 mol% water–HOAc mixture. It

Table 3 Co- and terpolymerization reactions in water-AcOH, employing the neutral palladium chloride precursors 1a₅, 1a₆, 1b and 1c

Entry	Precatalyst	<i>t</i> h	Water/mol%	Productivity/ $kg_{(polyketone)} g_{(Pd)}^{-1} h^{-1}$	$M_{\rm n}/{ m kg}~{ m mol}^{-1}~{ m [mp/^{\circ}C]}$	Propene (%)	h-t Regioselectivity ^a (%)
CO-eth	ene copolymer	izatio	1 ^{<i>b</i>}				
1	1a5	1	65	12.20	15.3 [251]		
2	1a5	2	65	11.28			
3	1b	1	65	7.47			
4^c	1b	1	75	8.90	5.1 [247]		
5 ^c	1b	2	75	5.50			
6	1a ₆	1	65	4.49	18.0 [251]		
7	1a ₆	2	65	3.47			
8	1c	1	65	8.39			
9°	1c	1	75	9.10	>40.0 [256]		
10 ^c	1c	2	75	6.00			
CO-pro	opene copolym	erizati	on ^d				
11	1a5	2	65	1.77	0.33		62
12	1b	2	75	0.64	0.37		53
13	1a ₆	2	65	0.99	0.30		61
14	1c	2	75	0.73	0.55		55
CO-eth	ene-propene to	erpoly	merization ^{d, e}				
15	1a5	1	65	5.34			
16	1a5	3	65	3.99	10.1 [186]	16.6	
17	1b	1	75	5.51			
18	1b	3	75	4.37	6.6 [150]	26.6	
19	1a ₆	1	65	2.93			
20	1a ₆	3	65	1.19	9.5 [186]	13.2	
21	1c	1	75	6.45			
22	1c	3	75	3.57	13.1 [180]	24.1	

^{*a*} (Head to tail, h-t) regioselectivity given in %, based on ¹³C{¹H} NMR integration. ^{*b*} Catalytic conditions: amount of palladium, 0.0048 mmol; AcOHwater, 100 mL; $p(CO)/p(C_2H_4)$, 20/20 bar; temperature, 85 °C; stirring rate, 1200 rpm. ^{*c*} Catalytic precursor, 0.0048 mmol.^{3*f*} ^{*d*} Amount of palladium, 0.0048 mmol; propene, 33 g and constant CO pressure, 56 bar at 85 °C. ^{*c*} Propene, 20 g; $p(C_2H_4)$, 7 bar at 20 °C and constant CO pressure, 70 bar at 85 °C. is generally agreed that the water proportion in the water–AcOH mixture controls both the solvolysis of the neutral Pd hydrido chloride species (B, Scheme 6), which generates cationic Pd^{II} –H initiators (C, Scheme 6) and the solubility of the monomers (*i.e.* CO and olefins) in the reaction medium.^{13,14}

A perusal of the CO-ethene copolymerization results (Table 3) shows that precatalyt $1a_5$ is about three times more active than 1a₆ (Table 3, entry 1 vs. 6), outperforming 1b and 1c (entry 1 vs 3, 4 and 8, 9, respectively) which are known to be highly active for this type of reaction.^{3f} The same productivity trend was observed for catalytic reactions lasting 2 h, featured by a productivity drop in the second hour by *ca*. 7% (1 a_5), 38% (1b), 23% (1 a_6) and 34% (1c). One may therefore conclude that $1a_5$ is the most active and also the most stable copolymerization catalyst under the present experimental conditions. All precatalysts investigated produced strictly-alternating polyketones containing exclusively ketone endgroups (¹H NMR evidence) due to protonolysis of the palladium alkyl species (F, Scheme 6) by water, leading to the formation of cationic Pd-OH species (I) that can regenerate a Pd^{II}-H initiator by the water gas shift reaction (WGS).¹⁵ Since 1a₅ and 1a₆ gave CO-ethene copolymers of similar average molecular weight, one may conclude that the chain transfer reaction (i.e. protonolysis) occurs at a comparable rate. In turn, this suggests that the metal centre in both catalysts exhibits comparable electrophilicity, hence similar propensity to promote Pd- β -hydride elimination of the Pd alkyl species (F. Scheme 6), which is the rate determining step of the protonolysis reaction.¹⁶ The different overall conformation of the o-MeO-dppcb ligand in the stereochemically rigid complexes 1a. and 1a₆, combined with possible Pd-o-MeO-oxygen interactions, may account for the slower propagation rate of the reaction catalyzed by the latter complex.

The same precursors have been employed to catalyse the CO– propene copolymerization reaction in the presence of a fixed amount of propene (33 g) and a constant CO feed during the catalytic process, using the same water–AcOH mixture composition of the analogous CO–ethene copolymerization reactions (Table 3, entries 11–14). Irrespective of the catalyst precursor, highly viscous copolymers with only poly(1-oxo-2-methyltrimethylene) units in the polymer chain were obtained. The ¹H and ¹³C{¹H} NMR characterization of the CO–propene copolymers in CDCl₃ showed the simultaneous presence of ketone (K) and vinyl (V) end groups (Scheme 7).

On the basis of integration of the corresponding ¹H NMR signals, $1a_5$, $1a_6$, 1b and 1c were assigned vinyl (V) to ketone (K) ratios of 7 : 33, 6 : 33, 3 : 33 and 1 : 33, respectively. As for the productivity of the CO–ethene copolymerization reactions, $1a_5$ showed again the highest performance within the series of precatalysts studied (entry 11 *vs.* 12–14) (Table 3).

The regioselectivity of the propene insertion (*i.e.* 1,2 or 2,1 insertion) into the growing polymer chain was determined by ${}^{13}C{}^{1}H{}$ NMR spectroscopy integrating the ${}^{13}C{}^{1}H{}$ CO signals, stemming from tail to tail (t-t), head to tail (h-t) and head to head (h-h) regioisomers (Scheme 8).¹⁷

Scheme 8

The stereochemically rigid binuclear palladium catalysts showed a significantly enhanced regioselectivity for the h-t regioisomer

Scheme 6

as compared to the mononuclear complexes (Table 3, entries 11 and 13 *vs.* 12 and 14). However, we do not have any clear-cut explanation for this result which other authors have previously observed and attributed to a complex web of steric and electronic factors.¹⁸

The present palladium precursors were also used to catalyse the terpolymerization reaction of CO-ethene and propene in the water-AcOH mixtures employed in the CO-ethene copolymerization reactions. The catalytic reactions were carried out in the presence of a fixed amount of propene (20 g) and ethene (7 bar) at 20 °C. The results of the catalytic study are reported in Table 3 (entries 15-22). Low-melting terpolymers were obtained with all precursors. The precursors $1a_5$ and $1a_6$ gave terpolymers characterized by a significantly lower propene incorporation as compared to 1b and 1c. In particular, 1b gave the terpolymer with the lowest melting point (150 °C), consistent with the lowest average molecular weight of the terpolymer and the highest content of propyl units (Table 3). The end-group analysis of the terpolymers showed the occurrence of the same type of endgroups observed for the CO-propene copolymers, confirming that the Pd-β-hydride elimination in Pd alkyl compounds containing an isopropylene unit attached to palladium is favoured over that in compounds containing an ethylene unit.^{17a} Complexes 1c and $1a_6$ showed the highest and lowest terpolymer productivity, respectively, while 1a₅ and 1b exhibited a comparable productivity (Table 3).

Conclusions

The reaction of the tetraphosphane *o*-MeO-dppcb with metal dichloride precursors of the Ni triad gives stereoselectively Pt^{II} and Ni^{II} binuclear complexes characterized by 5-4-5- and a 6-4-6-membered tricyclic ring systems, respectively. Conversely, Pd^{II} forms, under comparable experimental conditions, the linkage-isomeric compounds $1a_5$ (*i.e.* 5-4-5-membered ring system) and $1a_6$ (*i.e.* 6-4-6-membered ring system) in a *ca.* 4 : 1 isomeric ratio. This ratio was almost reversed by exploiting the template effect of Cr^{III} for the 6-4-6-membered ring system and the smooth substitution of Cr^{III} by Pd^{II}.

Compounds $1a_5$ and $1a_6$ have been employed to catalyse the CO– ethene and CO–propene copolymerization and the CO–ethene– propene terpolymerization in water–AcOH solvent mixtures with a prevalent water content (65–75 mol%). An analogous study was carried out with the mononuclear Pd^{II} complexes 1b and 1c.

The results obtained have shown that $1a_5$ is significantly more active than $1a_6$, outperforming the mononuclear precursors 1b and 1c which are known to generate the most active catalysts for CO– alkene copolymerization and terpolymerization reactions.³ The different catalytic activity of $1a_5$ and $1a_6$, along with the formation of polyketones with comparable average molecular weight, may be rationalized by the different overall conformation of the *o*-MeO-dppcb ligand in these complexes, which would influence the propagation step of the copolymerization. Finally, it is worth mentioning that while $1a_5$ and $1a_6$ favour, more than 1b and 1c, the head to tail regioselectivity of propene insertion into the growing polymer chain, they insert less propene in the growing terpolymer chain, mainly due to the higher steric demand of propene compared to ethene.

Experimental

Materials and physical measurements

All reactions and manipulations were carried out under a nitrogen atmosphere by using Schlenk-type techniques. The solvents were generally distilled over dehydrating reagents and were deoxygenated before use. The reagents were used as purchased from Aldrich, Fluka or Strem Chemicals. Bis(2methoxyphenyl)phosphane⁷ [PdCl₂(η⁴-COD)]¹⁹, [PdCl₂(P-P)] (P-P = o-MeO-dppe, o-MeO-dppp)^{3f} were prepared according to literature methods. The irradiation experiment has been carried out with an high pressure Hg-vapour UV-lamp. Co- and terpolymerization reactions were performed with a 320 ml stainless steel autoclave, constructed at the ICCOM-CNR (Florence, Italy), equipped with a magnetic drive stirrer and a Parr 4842 temperature and pressure controller. The autoclave was connected to a gas reservoir to maintain a constant pressure while performing the catalytic reactions. GC-MS analyses of the solutions were performed on a Shimadzu QP 5000 apparatus equipped with a SPB-1 Supelco fused silica capillary column (30 m, 0.25 mm i.d., 0.25 µm film thickness). Deuterated solvents for routine NMR measurements were dried over molecular sieves. ${}^{1}H$, ${}^{13}C{}^{1}H$, ³¹P{¹H} NMR spectra were obtained on a Bruker Avance DPX 300 spectrometer, measuring at 300.13, 75.48 and 121.50 MHz, respectively. Chemical shifts are reported in ppm (δ) with reference to either TMS as an internal standard (1H and 13C NMR) or 85% H₃PO₄ as an external standard (³¹P NMR). CP-MAS ³¹P NMR spectra were recorded at room temperature on a Bruker Avance DRX-400 spectrometer equipped with a 4 mm BB CP-MAS probe at a working frequency of 161.98 MHz. The spectra were recorded using a cross polarization pulse sequence under magic angle spinning at a spinning rate of 8.0 kHz. Elemental analyses were performed using a Perkin Elmer Model 2400 C,H,N elemental analyser. XRPD spectra were acquired at room temperature with a Bruker D8-Advance diffractometer, employing Cu Ka radiation $(\lambda = 1.5418 \text{ Å})$ and a scanning range between 2.5 and 80.0° with an acquisition step of 0.030° per second. Infrared spectra were recorded on a Nicolet 5700 ATR FTIR spectrometer. ESI-MS spectra were obtained on a Finnigan MAT-95 spectrometer, using 3-nitrobenzylalcohol (NOBA) as matrix. Structural optimizations were carried out applying the hybrid density functional theory (DFT) using the Gaussian 03 suite of programs.^{20a} The method used was the Becke's three-parameter hybrid exchange-correlation functional^{20b} containing the non-local gradient correction of Lee, Yang and Parr (B3LYP).^{20c} Calculations of the frequencies were performed to validate the nature of the optimized stationary points. The Stuttgart/Dresden effective core potential was used for metals.^{20d} The basis set used for the remaining atomic species was the 6-31G(d, p).^{20e}

Preparations

Synthesis of *o*-MeO-*trans*-dppen. A solution of *n*-BuLi (56.0 ml, 140.000 mmol) was added drop wise to a clear THF solution (1 l) of bis(2-methoxyphenyl)phosphane⁷ (24.6 g, 99.959 mmol) at room temperature, during which time interval the reaction solution turned orange followed by the precipitation of the yellow Li salt of the phosphane. The obtained suspension was allowed to stir for 1 h at 42 °C. Then 1,2-*trans*-dichlorethylene

(3.87 ml, 50.000 mmol) was slowly added at the latter temperature. Once the addition was complete an orange solution was obtained which was heated at 62 °C for 1 h to complete the reaction. Then the reaction solution was cooled to room temperature, guenched with water (3.5 ml) and evaporated to dryness. The slightly yellow residue was subjected to an extraction with CH₂Cl₂-H₂O. The organic phase was concentrated to dryness and the residue was washed with ethanol (150.0 ml), followed by its filtration with a Durapore^(R) membrane filter. The crude product was then recrystallized from CH₂Cl₂-MeOH (v/v 1.6 : 1), obtaining a white product which was separated by filtration and dried under vacuum. Yield: 13.9% (3.59 g, 6.954 mmol). C₃₀H₃₀O₄P₂ (516.23): calc. C, 69.76; H, 5.85; found: C, 69.63; H, 5.93%. ¹H NMR (CD₂Cl₂, 300.13 MHz, ppm): δ 3.76 (s, 12H, OCH₃), 6.40 (t, ²J_{PH} = 36 Hz, 2H, CH=CH), 6.88 (br s, 8H, Ar-H), 7.00 (br s, 4H, Ar-H), 7.32 (t, ${}^{3}J_{\rm PH} = 12$ Hz, 4H, o-Ar-H). ${}^{13}C{}^{1}H{}$ NMR (CD₂Cl₂, 75.48 MHz, ppm): δ 55.78 (s, OCH₃), 110.50 (s, Ar-C), 121.16 (s, Ar-C), 124.66 $(d, {}^{1}J_{PC} = 13 \text{ Hz}, \text{Ar-}C), 130.52 (s, \text{Ar-}C), 133.83 (s, \text{Ar-}C), 139.20$ $(t, {}^{1}J_{PC} = 36 \text{ Hz}, CH=CH), 161.60 (t, {}^{2}J_{PC} = 16 \text{ Hz}, C-OCH_{3}).$ ³¹P{¹H} NMR (CD₂Cl₂, 121.50 MHz, ppm): δ –29.20 (s).

Synthesis of *o*-MeO-dppcb. [PtCl₂(η^4 -COD)] (3.74 g, 9.998 mmol) was added to a deaerated solution of o-MeOtrans-dppen (5.16 g, 9.995 mmol) in CH₂Cl₂ (200 mL) at room temperature. The reaction mixture was allowed to stir for 4 h at room temperature. The white solid that was formed during the course of the reaction was separated by filtration and washed with CH_2Cl_2 (3 × 50 mL). After the latter solid had been suspended in deareated DMF (300 mL) and transferred to a Schlenk tube. the suspension was irradiated for 21 days. Then the solid which had formed was separated by filtration, washed with CH_2Cl_2 (3 × 50 mL) and re-suspended in deareated DMF (200 mL). To this suspension was added NaCN (3.67 g, 75.00 mol) dissolved in H₂O (10 mL), followed by heating the reaction mixture under nitrogen and stirring at 115 °C for 10 h. Afterwards the solvent mixture (i.e. H₂O and DMF) was removed completely by means of a vacuum pump and the residue was washed with H₂O (130 mL). The obtained crude product was dissolved in deareated CH₂Cl₂ (35 mL) and filtered. The clear CH₂Cl₂ solution was concentrated to a volume of 20 mL and on addition of diethyl ether (150 mL) the product precipitated as a white micro-crystalline powder, that was separated by filtration, washed with diethyl ether and dried under vacuum. Yield: 76.4% (3.94 g, 3.818 mmol). C₆₀H₆₀O₈P₄ (1033.01): calc. C, 69.76; H, 5.85; found: C, 69.61; H, 5.95%. ¹H NMR (CD₂Cl₂, 300.13 MHz, ppm): δ 3.57 (s, 24H, OCH₃), 3.43 (m, 4H, PCH), 6.57 (m, 8H, Ar-H), 6.64 (m, 8H, Ar-H), 6.99 (m, 8H, Ar-H), 7.08 (m, 8H, Ar-H). ${}^{13}C{}^{1}H{}$ NMR (CD₂Cl₂, 75.48 MHz, ppm): δ 38.50 (br s, PCH), 55.63 (s, OCH₃), 110.21 (s, Ar-C), 120.53 (s, Ar-C), 125.76 (d, ${}^{1}J_{PC} = 20$ Hz, Ar-C), 129.31 (s, Ar-C), 134.77 (s, Ar-C), 161.54 (d, ${}^{2}J_{PC} = 18$ Hz, COCH₃). $^{31}P{^{1}H} NMR (CD_2Cl_2, 121.50 MHz, ppm): \delta - 25.8 (s). ^{31}P{^{1}H}$ NMR (CD₂Cl₂, 121.50 MHz, -93 °C, ppm): δ -20.4 (br s), -37.2 (br s).

Reaction of *o*-MeO-dppcb with [PdCl₂(η^4 -COD)]: Synthesis of the linkage isomers 1a₅ and 1a₆. [PdCl₂(η^4 -COD)] (38.7 mg, 0.136 mmol) dissolved in deaerated CH₂Cl₂ (30 mL) was added to *o*-MeO-dppcb (70.0 mg, 0.068 mmol) and the obtained solution was allowed to stir for 30 min at room temperature, at the end of which a white product precipitated. The reaction was completed after an additional reaction time of 24 h maintaining the same reaction temperature. Then the white CH_2Cl_2 -insoluble product **1a**₅ was removed by filtration and washed with CH_2Cl_2 (2 × 10 mL). Yield (**1a**₅): 81% (76.4 mg, 0.055 mmol). $C_{60}H_{60}Cl_4O_8P_4Pd_2$ (1387.64): calc. C 51.93, H 4.32; found C 51.85, H 4.45%. CP-MAS ³¹P NMR (161.98 MHz, ppm): δ 44.60.

The combined CH_2Cl_2 phases (*i.e.* mother liquor and washing phase) were concentrated to dryness and a ³¹P{¹H} NMR spectrum thereof acquired in CD_2Cl_2 revealed **1a**₆ as the only phosphorus containing compound. Yield (**1a**₆): 19% (17.9 mg, 0.0129 mmol). For further characterization of **1a**₆ *vide infra*.

Alternative synthesis of $1a_6$. [PdCl₂(η^4 -COD)] (55.4 mg, 0.194 mmol) was added in one portion to a deaerated suspension of compound $4a_6$ (144.9 mg, 0.097 mmol) in CH₂Cl₂ (45 mL) at room temperature. The colour of the reaction mixture changed immediately to yellow. After an additional reaction time of 20 h, the suspension was filtered and the residue washed with CH₂Cl₂ $(2 \times 10 \text{ mL})$. The combined CH₂Cl₂ solutions were concentrated to dryness to give $1a_6$ as a light green product which was suspended in *n*-hexane (10 mL), removed by filtration and then dried under vacuum. Yield (1a₆): 74% (99.9 mg, 0.072 mmol). C₆₀H₆₀Cl₄O₈P₄Pd₂ (1387.64): calc. C 51.93, H 4.32; found C 51.80, H 4.47%. ¹H NMR (CD₂Cl₂, 300.13 MHz, ppm): δ 2.84 (m, 12H, OCH₃), 3.35 (br s, 12H, OCH₃), 3.94 (br s, 4H, CH), 6.23-7.54 (m, 30H, Ar-H), 9.06 (br s, 2H, o-Ar-H). ³¹P{¹H} NMR (CD₂Cl₂, 121.50 MHz, ppm): δ 17.80 (br s), 36.16 (br s). MS (ESI+) m/z: 1352.8 (M⁺ – Cl + H). CP-MAS ³¹P NMR (161.98 MHz, ppm): δ 17.94 (s), 38.00 (s).

The CH_2Cl_2 insoluble product was dried under vacuum and then subjected to elemental analysis and a XRPD measurement, which confirmed the occurrence of $1a_5$ as the only compound. Yield $(1a_5)$: 26% (35.0 mg, 0.025 mmol).

[Pt₂Cl₄(μ-(κP^1 , κP^2 ; κP^3 , κP^4 -*o*-MeO-dppcb))] (2a₅). [PtCl₂(η⁴-COD)] (36.2 mg, 0.096 mmol) was added to a deaerated CH₂Cl₂ solution (10 mL) of *o*-MeO-dppcb (50.0 mg, 0.048 mmol) at room temperature, causing precipitation of the product as a white powder. The suspension was allowed to stir for 1 h at room temperature. The white solid was then removed by filtration, washed with CH₂Cl₂ (2 × 5 mL) and dried under vacuum. The combined organic CH₂Cl₂ phases were concentrated to dryness, yielding no residue, thus indicating that **2a**₅ was the only compound formed in the course of the reaction. Yield: 98% (73.6 mg, 0.047 mmol). C₆₀H₆₀Cl₄O₈P₄Pt₂ (1565.00): calc. C 46.05, H 3.83; found C 45.93, H 3.97%. CP-MAS ³¹P NMR (161.98 MHz, ppm): δ 20.29 (¹*J*(PtP) 3717 Hz).

[Ni₂Cl₄(μ -(κP^1 : κP^2 : κP^3 : κP^4 -o-MeO-dppcb))] (3a₆). NiCl₂· 6H₂O (57.0 mg, 0.240 mmol), dissolved in a deaerated (5 : 1, v/v) solvent mixture of ethanol–water (50 mL), was added to a deaerated solution of o-MeO-dppcb (124.0 mg, 0.120 mmol) dissolved in CH₂Cl₂ (5 mL). The obtained suspension (*i.e.* o-MeO-dppcb precipitated out of the solvent mixture due to its low solubility in the latter reaction medium) was allowed to stir for 4 h, followed by the concentration of the obtained clear dark-red solution to dryness by means of a vacuum pump. The red compound was recrystallized from CH₂Cl₂ and dried under vacuum. The NMR spectroscopic study revealed **3a**₆ as the only phosphorus containing compound obtained during the course of the reaction. Yield 93% (144.2 mg, 0.112 mmol). $C_{60}H_{60}Cl_4Ni_2O_8P_4$ (1292.22): calc. C 55.77, H 4.64; found C 55.83, H 4.75%. ¹H NMR (CD₂Cl₂, 300.13 MHz, ppm): δ 1.14 (s, 3H, OCH₃), 1.53 (s, 3H, OCH₃), 2.78 (s, 6H, OCH₃), 3.02 (br s, 4H, CH), 3.41 (s, 6H, OCH₃), 4.26 (s, 6H, OCH₃), 6.19–7.40 (m, 30H, Ar-H), 9.60 (br s, 1H, *o*-Ar-H), 10.48 (br s, 1H, *o*-Ar-H). ³¹P{¹H} NMR (CD₂Cl₂, 121.50 MHz, ppm): δ 7.37 (d, ²J(PP) 94.0 Hz), 25.55 (d, ²J(PP) 94.0 Hz). MS (ESI+) *m*/*z*: 1255.0 (M⁺ – HCl – Cl).

 $[Cr_2Cl_6(THF)_2(\mu-(\kappa P^1:\kappa P^2:\kappa P^3:\kappa P^4-o-MeO-dppcb))]$ $(4a_6)$. CrCl₃(THF)₃ (58.0 mg, 0.154 mmol) was added to a deaerated solution of o-MeO-dppcb (80.0 mg, 0.077 mmol) in CH₂Cl₂ (30 mL) and allowed to stir for 10 h at room temperature giving a pink solution. Afterwards, the solvent was removed by vacuum, giving a pink product, which was used without further purification. NMR spectroscopic data of a CD₂Cl₂ solution of the isolated product are in accordance with the formation of $4a_6$ as the only product. Yield: 85% (97.8 mg, 0.065 mmol). C₆₈H₇₆Cl₆Cr₂O₁₀P₄ (1493.95): calc. C 54.67, H 5.08; found 54.53, H 5.33%. ¹H NMR (CD₂Cl₂, 300.13 MHz, ppm): δ 1.84 (br s, 8H, THF), 2.86 (br s, 8H, THF), 3.62 (br m, 24H, OCH₃), 4.10 (br m, 4H, CH), 6.22–7.74 (br m, 32H, Ar-H). ³¹P{¹H} NMR (CH₂Cl₂, 121.50 MHz, ppm): δ –12.13 (s). MS (ESI+) m/z: 1525.2 (M⁺ + MeOH - H).

 $[Pd_2(OAc)_4(\mu-(\kappa P^1,\kappa P^2:\kappa P^3,\kappa P^4-o-MeO-dppcb))]$ (5a₅). Silver acetate (37.0 mg, 0.220 mmol) was added to a deaerated suspension of 1a₅ (76.9 mg, 0.055 mmol) in acetonitrile (30 mL) at room temperature. The reaction mixture was stirred for 14 h at room temperature. Afterwards the suspension was filtered and the residue washed with acetonitrile $(2 \times 10 \text{ mL})$, followed by the evaporation of the solvent to dryness by means of a vacuum pump, obtaining the product as a yellow powder, that was recrystallized from CH₂Cl₂-diethyl ether and then dried under vacuum. Yield: 51% (41.6 mg, 0.028 mmol) C₆₈H₇₂O₁₆P₄Pd₂ (1482.02): calc. C 55.11, H 4.85; found C 55.02, H 4.95%. ¹H NMR (CD₂Cl₂, 300.13 MHz, ppm): δ 1.10 (br s, 12H, CO₂CH₃), 2.79 (s, 12H, OCH₃), 3.53 (s, 12H, OCH₃), 4.17 (d, ³J(HH) 4.0 Hz, 2H, CH), 4.19 (d, ³J(HH) 4.0 Hz, 2H, CH), 6.69–7.67 (m, 30H, Ar-H), 8.81 (br s, 2H, Ar-H). ¹³C{¹H} NMR (CD₂Cl₂, 75.48 MHz, ppm): δ 11.07 (s, CO₂CH₃), 14.20 (s, CO₂CH₃), 32.25 (s, CH), 55.85 (s, OCH₃), 56.19 (s, OCH₃), 111.98-135.12 (Ar-C), 161.62 (s, CO_2CH_3). ³¹P{¹H} NMR (CD_2Cl_2 , 121.50 MHz, ppm): δ 35.99 (s). MS (ESI+) m/z: 1423.2 (M⁺ – OAc). IR (KBr, v(COO)/cm⁻¹) 1584(m).

[Pd₂(OAc)₄(μ-($\kappa P^1:\kappa P^2:\kappa P^3:\kappa P^4$ -*o*-MeO-dppcb))] (5a₆). Silver acetate (64.9 mg, 0.388 mmol) was added to a deaerated suspension of 1a₆ (133.9 mg, 0.097 mmol) in THF (15 mL) at room temperature. The suspension was allowed to stir for 14 h at the same temperature, followed by its filtration to remove AgCl. The obtained solution was concentrated to dryness under vacuum and the greenish-yellow product was recrystallized from CH₂Cl₂-*n*hexane, filtered off and dried under vacuum. Yield: 25% (35.6 mg, 0.024 mmol). C₆₈H₇₂O₁₆P₄Pd₂ (1482.02): calc. C 55.11, H 4.85; found C 54.97, H 5.05%. ¹H NMR (CD₂Cl₂, 300.13 MHz, ppm): δ 1.89 (s, 6H, CO₂CH₃), 2.19 (s, 6H, CO₂CH₃), 3.08 (br s, 12H, OCH₃), 3.28 (br. s, 12H, OCH₃), 4.09 (m, 4H, CH), 6.90–7.67 (m, 30H, Ar-H), 10.18 (br s, 2H, *o*-Ar-H). ¹³C{¹H} NMR (CD₂Cl₂, 75.48 MHz, ppm): δ 11.18 (s, CO₂CH₃), 14.24 (s, CO₂CH₃), 20.82 (s, CO₂CH₃), 21.23 (s, CO₂CH₃), 32.68 (s, CH), 34.93 (s, CH), 37.86 (s, CH), 39.74 (s, CH), 55.48 (s, OCH₃), 56.53 (s, OCH₃), 111.20–162.25 (Ar-C), 167.51 (s, CO₂CH₃), 169.44 (s, CO₂CH₃), 175.94 (s, CO₂CH₃). ³¹P{¹H} NMR (CD₂Cl₂, 121.50 MHz, ppm): δ 29.76 (s). MS (ESI+) *m/z*: 1422.90 (M⁺ – OAc). IR (KBr, *v*(COO)/cm⁻¹) 1573(m).

Catalytic co-and terpolymerization reactions

CO–ethene copolymerization reactions in water–AcOH with $1a_5$, $1a_6$, 1b and 1c as catalyst precursors. In a typical experiment, a deaerated solvent mixture of distilled water and AcOH (100 mL) was introduced by suction into an autoclave (320 mL), previously evacuated using a vacuum pump, containing the catalyst precursor (0.0024 mmol). The autoclave was charged with a 1 : 1 CO–ethene mixture to 21 bar at room temperature and then heated to $85 \,^{\circ}$ C, where the gas pressure was adjusted to 40 bar. The reaction was conducted under stirring (1200 rpm) at constant pressure, feeding the autoclave with a 1 : 1 CO–ethene gas-mixture from a gas reservoir. 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 water, and dried under vacuum at 60 °C to constant weight.

CO-propene copolymerization in water-AcOH with 1a₅, 1a₆, 1b and 1c as catalyst precursors. In a typical experiment, a deaerated mixture of distilled water and AcOH (100 mL) was introduced by suction into an autoclave (320 mL), previously evacuated using a vacuum pump, containing the catalyst precursor (0.0048 mmol of palladium). The autoclave was cooled to 0 °C, followed by charging it with propene (33 g) and warming it to 20 °C. At this latter temperature the autoclave was charged with CO (7 bar), followed by heating it to 85 °C. Stirring (1200 rpm) was started as soon as the latter temperature had been reached and the reaction was conducted at a constant pressure of CO (56 bar), feeding the autoclave with CO, derived from a gas reservoir. After a reaction time of 2 h, the autoclave was cooled to room temperature by means of an ice-water bath and the unreacted gases were released. The viscous MeOH solution of the oligomeric material was evaporated at 50 °C by means of a vacuum pump to reach constant weight of the cooligomers.

CO-ethene-propene terpolymerization in water-AcOH with $1a_5$, $1a_6$, 1b and 1c as catalyst precursors. In a typical experiment, a deaerated solvent mixture of distilled water and AcOH (100 mL) was introduced by suction into an autoclave (320 mL), previously evacuated using a vacuum pump, containing the catalyst precursor (0.0048 mmol of palladium). The autoclave was cooled to 0 °C, followed by charging it with propene (20 g). Then the autoclave was warmed to 20 °C and successively charged with ethene (7 bar) and CO (7 bar), followed by heating to 85 °C. At this latter temperature the total gas pressure was adjusted with CO to 70 bar and the reaction was conducted under stirring (1200 rpm) and constant CO pressure, feeding the autoclave with CO derived from a gas reservoir. 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 terpolymers were filtered off,

Table 4Crystallographic data for 1a6.2.8DCE and 2a5

	1a ₆ ·2.8DCE	2a ₅
Empirical formula	$C_{656}H_{71}Cl_{960}O_8P_4Pd_2$	$C_{60}H_{60}Cl_4O_8P_4Pt_2$
Formula weight	1657.37	1564.92
T/K	243(2)	243(2)
λ/Å	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1/n$	Tetragonal, $P4_22_12$
a/Å	12.3220(4)	15.2961(2)
b/Å	12.3410(3)	15.2961(2)
c/Å	46.7560(10)	12.4875(3)
$\beta/^{\circ}$	90.568(1)	90
$V/Å^3$	7109.6(3)	2921.71(11)
Ζ	4	2
$D_{\rm c}/{ m Mg}{ m m}^{-3}$	1.548	1.779
μ/mm^{-1}	1.008	5.130
F(000)	3347	1536
Crystal size/mm	$0.10 \times 0.05 \times 0.03$	$0.10 \times 0.09 \times 0.04$
Absorption correction	MULTI-SCAN	MULTI-SCAN
Reflections collected (R_{int})	23218 (0.0290)	26282 (0.0313)
Θ -range for data collection/°	0.99–25.40	0.99–27.59
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameter	12414/2/834	3135/0/180
Goodness-of-fit on F^2	0.976	0.995
Final <i>R</i> indices	$[I > 3\sigma(I)] R1 = 0.0575, wR2 = 0.1317$	$[I > 2\sigma(I)] R1 = 0.0263, wR2 = 0.0575$
R indices (all data)	R1 = 0.0944, wR2 = 0.2078	R1 = 0.0340, wR2 = 0.0665
Largest diff. peak, hole/eÅ ³	0.640, -0.510	0.570, -0.330

washed with water and then dried at room temperature by means of a vacuum pump to reach a constant weight of the terpolymers.

Characterization of the CO–ethene, CO–propene copolymers and the CO–ethene–propene terpolymers. The alternating CO– ethene copolymers have been analysed by ¹H and ¹³C{¹H} NMR spectroscopy, carried out in a 1 : 1 (v/v) solvent mixture of 1,1,1,3,3,3-hexafluoroisopropanol- d_2 and C₆D₆. ¹H and ¹³C{¹H} NMR signals were assigned based on literature reports,^{3/,5} and the molecular weight determination was based on integration of the corresponding ¹H signals.^{3/}

The alternating CO-propene cooligomers and CO-ethenepropene terpolymers have been analysed by ¹H and ¹³C $\{^{1}H\}$ NMR spectroscopy carried out in CDCl₃ as well as by IR spectroscopy. The ratio of the regioisomeric propene incorporation was determined upon integration of the corresponding ¹³C{¹H}NMR signals (carbonyl region), deriving from h-h, h-t and t-t regioisomers,17 while the amount of propene incorporated in the terpolymers was determined by integration of the corresponding ¹H 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-ethenepropene terpolymers are: 2967 (w), 2935 (w), 2904 (w), 1701 (s), 1458 (w), 1394 (m), 1379 (m), 1360 (m) and 1085 (m) cm⁻¹. The average molecular weight of the CO-propene copolymers and of the CO-ethene-propene terpolymers have been determined by integration of the corresponding ¹H NMR signals.

X-Ray crystallographic data collection and refinement of the structures

The crystallographic data for $1a_6$ -2.8DCE and $2a_5$ are summarized in Table 4. Graphite-monochromated Mo-K α radiation ($\lambda=0.71073$ Å) was used. The data collection was performed on

a Nonius Kappa CCD diffractometer using φ - ω -scans. Cell refinement, data reduction and empirical absorption correction were carried out with the Denzo and Scalepack programs.^{21a} All structure determination calculations were performed with SHELXTL NT V6.1 including SHELXS-97 and SHELXL-97.^{21b} Final refinements on F^2 were carried out with anisotropic thermal parameters for all non-hydrogen atoms. For **2a**₅, the proton attached to the cyclobutane carbon ring was located and isotropically refined with fixed *U*. All other hydrogen atoms were included in the refinement using a riding model with isotropic *U* values depending on the U_{eq} of the adjacent carbon atoms. Two out of three DCE solvent molecules of the asymmetric unit of structure **1a**₆·2.8DCE are disordered. CCDC reference number for **1a**₆·2.8DCE: 694967 and **2a**₅: 694966.

Acknowledgements

The authors thank Dr P. Barbaro for the assistance in the acquisition of CP-MAS ³¹P NMR spectra. Thanks are also due to the European Commission for financing the project IDECAT, NoE contract no. NMP3-CT-2005-011730. Furthermore A. I. kindly acknowledges CINECA for the computing time provided in agreement with CNR. This research was financially supported by the Fonds zur Förderung der wissenschaftlichen Forschung, Vienna, Austria, the Tiroler Wissenschaftsfonds, Innsbruck, Austria, and the University of Innsbruck *via* the action D. Swarovski & Co.

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