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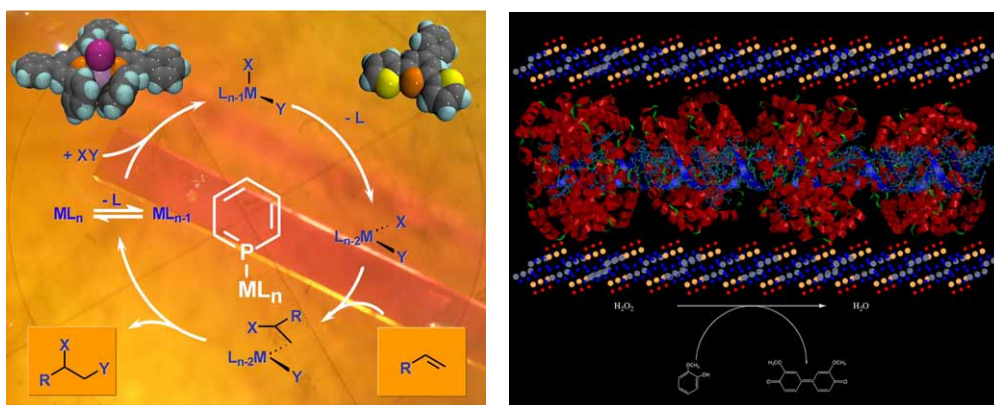
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Ligand effects in the non-alternating CO–ethylene copolymerization by palladium(II) catalysis†

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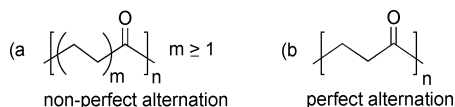
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In this paper we report on a comparative study of the non-alternating CO–C₂H₄ copolymerization catalyzed by neutral Pd^{II} complexes with the phosphine–sulfonate ligands bis(*o*-methoxyphenyl)-phosphinophenylenesulfonate and bis(*o*-methoxyphenyl)phosphino-ethylenesulfonate. The former ligand, featuring a lower skeletal flexibility, has been found to form more active catalysts as well as produce polyketones with higher molecular weight and higher extra-ethylene incorporation. *Operando* high-pressure NMR studies have allowed us to intercept, for the first time, Pd^{II}(phosphine–sulfonate) β-chelates in the non-alternating copolymerization cycle, while model organometallic reactions have contributed to demonstrate that Pd^{II} (phosphine–sulfonate) fragments do not form stable carbonyl complexes. The opening of the β-chelates has been found to be a viable process by either comonomer, which contrasts with the behaviour of Pd^{II} (chelating diphosphine) catalysts for the perfectly alternating copolymerization.

Introduction

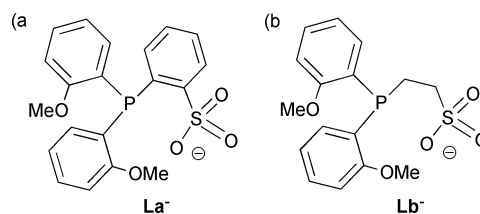
Copolymers of ethylene and carbon monoxide can exist either with the non-alternating structure (Scheme 1a) or with the perfectly alternating structure (Scheme 1b). Polyketones with the latter structure are invariably produced by insertion polymerization processes for which palladium(II) complexes supported by chelating diphosphine ligands generate by far the most efficient catalytic systems.¹ In contrast, non-alternating copolymers can be obtained by either free radical² or insertion polymerization reactions.³



Scheme 1

The known catalysts for non-alternation by insertion polymerization are based on palladium(II) salts modified with anionic chelating ligands bearing phosphorus and oxygen donor atoms (P ~ O[−]). An example of these ligands, primarily described by Drent,^{3a} is shown in Scheme 2a.

Following Drent's discovery, other authors have demonstrated the effectiveness of such P ~ O[−] ligands in the non-alternating CO–C₂H₄ copolymerization and their studies, both experimental^{3a–c} and theoretical,^{3d,e} have contributed to shed light onto the factors responsible for the non-alternation. From an experimental point



Scheme 2

of view, it is agreed that the non-alternation of co-monomers is promoted by high temperatures (> 100 °C) and low partial pressures of CO in the feed. Much less consensus has been reached on the stereoelectronic factors that favour non-alternation over perfect alternation. Some authors suggest that non-alternation is a result of facile decarbonylation of Pd acyl species with no intermediacy of β-chelates;^{3d,e} other authors propose that multiple ethylene insertion is just facilitated by the destabilization of neutral β-chelates.^{3a–c}

At present, the catalysts producing non-alternating copolymers are nearly two orders of magnitude less active than those producing strictly alternating copolymers. New catalytic systems should therefore be designed to increase the productivity, which is still a relevant goal since non-alternating polyketones exhibit lower melting points as compared to perfectly alternating materials.^{3a,b}

In this paper we report on a study of the non-alternating CO–C₂H₄ copolymerization by palladium(II) catalysis where the catalytic activity promoted by the Drent's bis(*o*-methoxyphenyl)-phosphinophenylenesulfonate ligand (La[−]) is compared to that of the recently synthesized bis(*o*-methoxyphenyl)phosphinoethylenesulfonate ligand⁴ (Lb[−]) (Scheme 2b). For the first time, the non-alternating CO–C₂H₄ copolymerization has been investigated by means of batch catalytic reactions, *operando* high-pressure NMR experiments and model organometallic reactions. We are confident that the gathered structural and mechanistic information will

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†CCDC reference number for 2b: 653758. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b711280g

be useful in designing improved catalytic systems for the non-alternating CO–C₂H₄ copolymerization.

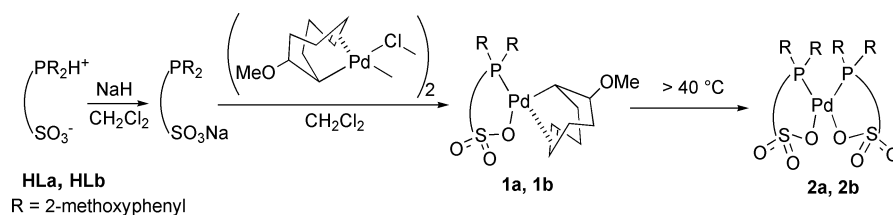
Results and discussion

Synthesis and characterization of the catalyst precursors

Instead of using the *in situ* procedure reported by Drent to generate the copolymerization catalyst, *i.e.*, the addition of a slight excess of ligand to a MeOH solution of Pd(OAc)₂,^{3a} we decided to synthesize well-defined Pd^{II} alkyl precursors. Indeed, only structurally defined precursors would have allowed us to draw out reliable information from the model and *operando* studies. One of the synthetic protocols adopted, primarily described by Rieger,^{3b} is shown in Scheme 3. The sodium salt of the appropriate zwitterionic P ~ O ligand, either 2-{bis(2-methoxyphenyl)phosphonium}benzenesulfonate^{3a} (**HLa**) or 2-{bis(2-methoxyphenyl)phosphonium}ethylenesulfonate⁴ (**HLb**), was reacted in CH₂Cl₂ at room temperature with the palladium complex [Pd(μ-Cl)(η¹,η²-codyl*)]₂ (codyl* = 2-methoxycyclooct-5-enyl).⁵ As a result, the neutral palladium complexes Pd(η¹,η²-codyl*)(La) (**1a**) and Pd(η¹,η²-codyl*)(Lb) (**1b**) were obtained in good yield and were characterized in solution by multinuclear NMR spectroscopy and in the solid state by elemental analysis (Scheme 3).

Compounds **1a** and **1b** are soluble in polar organic solvents (MeOH, CH₂Cl₂, THF) where they are moderately stable at room temperature. Above 40 °C, both complexes start decomposing with formation of palladium black and a palladium complex analysed as Pd(La)₂ (**2a**) or Pd(Lb)₂ (**2b**). However, while **2a** persisted as the major product in solution for several hours, **2b** rapidly disappeared. Unfortunately, the latter complex is insoluble in common organic solvents and its crystal dimensions were too small for reliable X-ray data collection. Therefore, the identification of **2b** was achieved indirectly by reacting Pd(OAc)₂ with two equivalents of Lb in CH₂Cl₂ mixture. The single crystals obtained could be studied by X-ray diffraction methods showing the complex to contain a palladium(II) centre coordinated by two ligands (*vide infra*). Since the elemental analysis data and IR spectra of the independently prepared complex are identical to those of **2b**, one may safely conclude that **1b** decomposes in solution yielding the Pd^{II} bis-chelate Pd(Lb)₂ (Scheme 3). The same considerations can be made for **2a** whose X-ray structure has been published elsewhere.^{3b}

Experimental X-ray diffraction parameters and selected bond length and distances for **2b** are reported in Tables 1 and 2, respectively, while an ORTEP drawing of the structure is shown in Fig. 1.



Scheme 3

Table 1 Crystallographic data for **2b**

Formula	C ₃₂ H ₃₆ O ₁₀ P ₂ PdS ₂
<i>M</i>	813.07
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁
<i>a</i> /Å	9.403(5)
<i>b</i> /Å	19.844(5)
<i>c</i> /Å	10.566(5)
<i>α</i> /°	90.0
<i>β</i> /°	114.647(5)
<i>γ</i> /°	90.0
<i>V</i> /Å ³	1791.9(14)
<i>D_c</i> /Mg m ⁻³	1.507
<i>Z</i>	2
<i>μ</i> /mm ⁻¹	0.777
<i>F</i> (000)	832
<i>λ</i> /Å	0.71073
<i>T</i> /K	293(2)
Measured reflections	2803
Unique reflections	2765
Refined parameters	428
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0299, <i>wR</i> 1 = 0.0827
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0306, <i>wR</i> 2 = 0.0832
<i>S</i> on <i>F</i> ²	1.081
Flack parameter	0.01(3)
Δρ _{min} /e Å ⁻³	−0.417
Δρ _{max} /e Å ⁻³	0.086

Table 2 Selected bond distances (Å) and angles (°) for **2b**

Pd(1)–P(1)	2.241(1)
Pd(1)–P(2)	2.340(1)
Pd(1)–O(5)	2.105(4)
Pd(1)–O(8)	2.103(4)
P(1)–Pd(1)–P(2)	102.97(6)
O(5)–Pd(1)–O(8)	87.29(17)
P(1)–Pd(1)–O(5)	85.30(12)
P(2)–Pd(1)–O(8)	84.44(13)
Intramolecular distances/Å	
Pd(1) ... O(1)	5.083(5)
Pd(1) ... O(2)	3.679(4)
Pd(1) ... O(3)	3.783(5)
Pd(1) ... O(4)	5.018(4)
Pd(1) ... H(9)	2.720
Pd(1) ... H(25)	2.756

The metal center in **2b** is square-planar coordinated by two *cis* phosphorus and sulfonato oxygen atoms belonging to two different P ~ O ligands.^{3b,6} Notably, a similar structure has been reported for the analogous La derivative, Pd(La)₂ (**2a**).^{3b}

The palladium atom in **2b** shows no significant deviation from the best coordination plane defined by the atoms P(1), P(2), O(5) and O(8). The molecule is C₂-symmetric with the C₂ axis bisecting

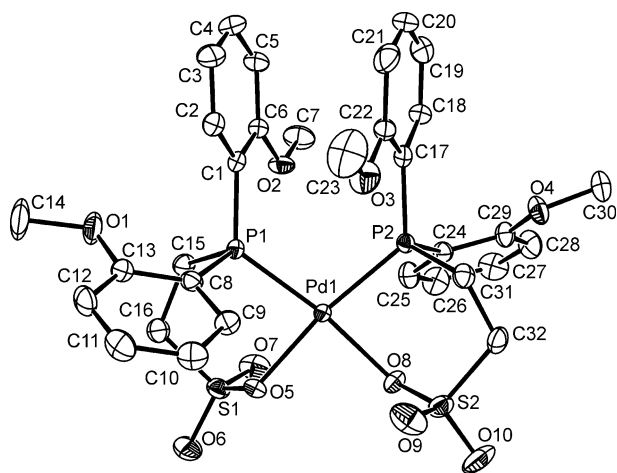


Fig. 1 ORTEP drawing of **2b**. Hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at a 30% probability level.

the P(1)–Pd(1)–P(2) angle of 102.97(6)°. The bite angles of each ligand are only slightly different from each other (85.30(12)° (P(1)–Pd(1)–O(5)) and 84.44(13)° (P(2)–Pd(1)–O(8)), and both Pd–O bonds are almost identical (2.105(4) Å for Pd(1)–O(5) and 2.103(4) Å for Pd(1)–O(8)). In contrast, the Pd–P bond lengths are significantly different from each other (2.241(1) Å for Pd(1)–P(1)) and 2.340(1) Å for Pd(1)–P(2)), which may be due to the steric congestion exerted by the two equatorial 2-methoxyphenyl units.

The distances between Pd and the *o*-methoxy oxygen atoms range from 3.679(4) Å to 5.083(5) Å and are thus far from being considered bonding interactions.⁷ In contrast, the Pd center exhibits distances of 2.720 Å (Pd(1)–H(9)) and 2.756 Å (Pd(1)–H(25)) from the *ortho* hydrogen atom belonging to the axial 2-methoxyphenyl units of each P ~ O ligand.

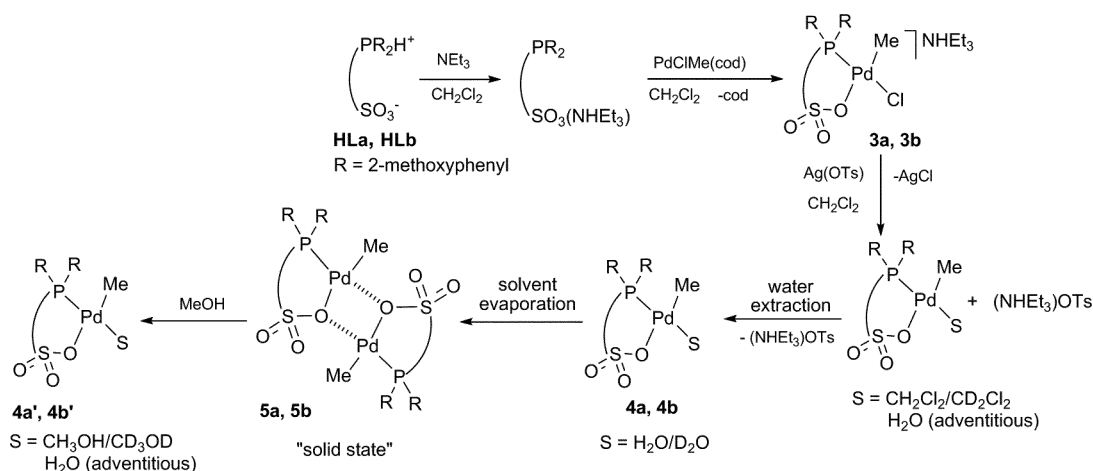
The anionic methylpalladium(II) complexes [PdClMe(La)](NH₄)⁺ (**3a**) and [PdClMe(Lb)](NH₄)⁺ (**3b**) were prepared by the reaction of the triethylammonium salt of **HLa** and **HLb** with PdClMe(cod). The overall synthetic procedure is summarized in Scheme 4.

Both complexes were isolated as off-white microcrystals and were satisfactorily characterized by multinuclear NMR spec-

troscopy and elemental analysis. Compounds **3a** and **3b** were transformed into the neutral derivatives Pd(H₂O)Me(La) (**4a**) and Pd(H₂O)Me(Lb) (**4b**), respectively, on treatment with AgOTs in CH₂Cl₂, followed by extraction of the (NH₄)OTs by-product with water. The identification of **4a**, **4b** was achieved *in situ* by ¹H and ³¹P{¹H} NMR spectroscopy. No evidence for an intermolecular agostic Pd–methyl–hydrogen interaction resulted from ¹H NMR spectra. Upon solvent elimination under reduced pressure, **4a** and **4b** were transformed into two different species, insoluble in CH₂Cl₂, for which we propose the binuclear structures [PdMe(La)]₂ (**5a**) and [PdMe(Lb)]₂ (**5b**) where two Pd(P ~ O) units are kept together by Pd–O bonds as shown in Scheme 4. Apparently, the water molecule in **4a** and **4b** is weakly bound to palladium so as to be easily removed under reduced pressure. In this eventuality, the unsaturated PdMe(P ~ O) fragment has no other choice than dimerization to get stabilized. It is noteworthy to recall that a quite similar binuclear structure has been reported for neutral [NiPh(P ~ O)]₂ complexes where P ~ O is a chelating phosphanylenolato ligand.⁹ Interestingly, the dissolution of **5a** and **5b** in MeOH gave the mononuclear methylpalladium complexes Pd(S)Me(La) (**4a'**) and Pd(S)Me(Lb) (**4b'**) where S may be either MeOH or adventitious H₂O, the latter being preferred for its greater binding affinity to Pd^{II} centers.¹⁰ Since the NMR spectra of **4a'** and **4b'** have been acquired in MeOH-*d*₄, a fast exchange between a possibly coordinated solvent molecule and the bulk solvent, would not allow for the observation of a coordinated solvent by ¹H spectroscopy. Compounds **5a** and **5b** dissolve also in CH₂Cl₂ containing nucleophiles such as pyridine or triphenylphosphine to give complexes with the formula Pd(L')Me(L) (L = **La**, **Lb**; L' = Py, PPh₃).^{3c} One may therefore conclude that the intramolecular Pd–O interaction that bridges the PdMe(P ~ O) moieties in **5a** and **5b** is very weak and can be broken up by any sort of nucleophile.

Catalytic copolymerization of CO and ethylene

The neutral Pd^{II} alkyl complexes **1a**, **1b**, **5a** and **5b** have been tested as catalyst precursors for the CO–C₂H₄ copolymerization either in MeOH or in TFE. The reaction temperatures of 120 °C (**1a/5a**) and 110 °C for (**1b/5b**) correspond to the maximum of



Scheme 4

Table 3 Non-perfectly alternating copolymerization of CO and ethylene catalyzed by **1a** and **5a**^a

Entry	Precat.	<i>t</i> /h	<i>T</i> /°C	C ₂ H ₄ /CO pressure/bar	C ₂ H ₄ /CO ratio	TsOH/BQ amount (equiv.)	Prod. ^b	Extra C ₂ H ₄ (%) ^c	Mp
1	1a	1	120	28.0/28.0	1		254	1.5	240
2 ^d	1a	1	120	28.0/28.0	1	0/80	490	1.1	
3	1a	1	110	42.0/14.0	3		153	3.2	230
4	5a	1	120	42.0/14.0	3		170	5.6	
5	1a	1	120	42.0/14.0	3		175	6.0	225
6	1a	1	120	42.0/14.0	3	20/0	90	5.8	
7	5a	1	120	42.0/14.0	3	20/0	101	5.9	
8 ^d	1a	1	120	42.0/14.0	3	0/80	337	4.4	228
9 ^{d,e}	1a	1	120	42.0/14.0	3		337	3.4	235
10 ^{d,e}	1a	1	120	42.0/14.0	3	0/80	607	2.9	
11	1a	1	120	48.0/8.0	6		125	9.9	220
12 ^d	1a	1	120	48.0/8.0	6	0/80	205	8.5	218
13	1a	1	120	53.3/2.7	20		41	27.8	193
14 ^d	1a	1	120	53.3/2.7	20	0/80	93	23.6	195
15 ^{d,e}	1a	1	120	53.3/2.7	20		77	23.8	
16 ^{d,e}	1a	1	120	53.3/2.7	20	0/80	130	20.2	196

^a Catalytic conditions: palladium, 0.012 mmol; *P*(total) at reaction temp., 56.0 bar; MeOH, 50 mL; stirring rate, 1300 rpm. ^b Productivity expressed as g(polyketone) (mmol(Pd) × h)⁻¹. ^c Total mol% of C₂H₄ involved in non-alternation, calculated from ¹³C{¹H} NMR spectra. ^d Palladium, 0.003 mmol. ^e TFE, 50 mL.

the catalytic productivity for each precursor. Different partial pressures of CO and C₂H₄ as well as the addition of co-reagents have been investigated. The results of this study are reported in Tables 3 and 4

Irrespective of the experimental conditions, the pre-catalysts with ligand **La** were much more active than those with the more flexible ligand **Lb** and also gave much higher molecular weight copolymers (*M_w* > 30 kg mol⁻¹)^{3a} (Tables 3–4). Likewise, irrespective of the pre-catalyst, the presence of an organic oxidant such as BQ had a beneficial effect on the productivity. Indeed, a drawback of any Pd^{II}-based catalyst for the CO–C₂H₄ copolymerization is its tendency to undergo irreversible reduction to Pd-species, precursor to palladium black. This degradation path is apparently more effective for **1b** than for **1a** (*vide infra*).

Besides adding an oxidant, the stability of catalysts in the CO–C₂H₄ alternating copolymerization can be increased by the co-presence of protic acids, generally TsOH, in the catalytic mixtures.¹ In the case of non-alternating processes, the role of the protic acid might be even more complex as it may protonate the sulfonato group, leading to the disruption of the chelating structure with consequent formation of less stable monodentate [HSO₃ ~ P(aryl)₂]Pd^{II} complexes. This negative action of the protic acid may account for the decreased productivity of the reactions catalyzed by **1a** and **5a** (entries 6 and 7, Table 3), whereas a positive effect seems to still prevail for the reactions catalyzed by **1b** (Table 4). In the latter case, the loss of stability due to the disruption of the chelate metalla-ring by the protic acid might be compensated by the positive action on the metal oxidation state.

The productivity decreased for all catalysts by decreasing the partial pressure of CO, which is in line with perfectly alternating CO–C₂H₄ copolymerizations by chelating diphosphine-Pd^{II} catalysis, except for those reactions where the catalysts are stabilized by chelating diphosphine bearing *o*-methoxy substituted aryl groups (zero-order dependence on CO pressure).^{7b,11}

Irrespective of the precatalyst as well as catalytic conditions, all non-alternating polyketones exhibit a linear polymeric chain (¹³C{¹H}NMR evidence) with no evidence of incorporation of ethylene oligomers that may form by ethylene oligomerisation.^{3a}

Indeed, **1b** has been found to oligomerize ethylene to butenes and traces of hexenes.

Notably, we have observed by ¹³C NMR spectroscopy that **1a** was capable of promoting the triple ethylene insertion,^{3a} whereas only double ethylene insertion was found in the materials obtained with **1b**.

As for the degree of ethylene extra-insertion, the catalysts containing the ligand **La** gave higher olefin incorporation than those with **Lb** under comparable experimental conditions. The degree of extra-insertion into the growing polyketone chain is controlled by several factors.^{3d,e} In agreement with previous reports, we have found that higher temperatures and lower partial pressures of CO, at constant total pressure, favour the extra enchainment of ethylene. The presence of BQ did not appreciably affect the degree of extra-insertion, while an increase of the latter was observed by adding TsOH to the reactions catalyzed by **1b**. As expected, the melting point of the polyketones decreased on increasing the amount of extra-ethylene insertion, for example from 230 °C with 3.2% extra-insertion (entry 3, Table 3) to 193 °C with 27.8% extra-insertion (entry 13, Table 3).

An end-group analysis was carried out on the polyketones obtained with **1b** as their molecular weight was sufficiently low to allow for a reliable ¹H NMR investigation in a 1 : 3 (v : v) mixture of HFIP-*d*₂ and C₆D₆. In the absence of added protic acid, three types of end-groups, namely ester (E), ketone (K) and vinyl (V), were observed in a 10 : 10 : 1 ratio, respectively, which means that chain transfer may occur by protonolysis, methanolysis or both of them. On the other hand, the observed keto-ester ratio and the results of the model studies in MeOH (*vide infra*, Scheme 5) suggest that the chain transfer occurs prevalently by methanolysis. The small but appreciable amount of vinyl end groups shows that also β-H elimination is a possible termination path. In the presence of acid, only ketone end groups were observed.¹

Replacing MeOH with TFE as reaction solvent increased the productivity, especially for the catalysts with the more rigid ligand **La** (entries 9 and 10 and 15 and 16, Table 3; entry 9, Table 4).^{7a,12} The beneficial effect of TFE on the catalytic activity is typical for CO–C₂H₄ copolymerization reactions due to the good solubility

Table 4 Non-perfectly alternating copolymerization of CO and ethylene catalyzed by **1b** and **5b**^a

Entry	Precat.	t/h	T/°C	C ₂ H ₄ /CO pressure/bar	C ₂ H ₄ /CO ratio	TsOH/BQ amount (equiv.)	Prod. ^b	M _n (kg × mol ⁻¹) ^c	Extra C ₂ H ₄ (%) ^d	Mp
1	1b	6	110	28.0/28.0	1	20/0	4.0		0.2	237
2	1b	6	100	42.0/14.0	3	80/0	1.3		0.2	
3	1b	6	110	42.0/14.0	3		0.4	5.3	0.3	
4	5b	6	110	42.0/14.0	3		0.4		0.3	
5	1b	6	110	42.0/14.0	3	20/0	1.9	5.2	3.0	
6	1b	6	110	42.0/14.0	3	80/0	5.4	5.4	6.6	229
7	1b	6	110	42.0/14.0	3	160/0	1.8	8.4	23.2	
8	1b	6	110	42.0/14.0	3	0/80	1.3	4.2	1.0	
9 ^e	1b	6	110	42.0/14.0	3		0.6	4.3	0.5	
10	1b	6	120	42.0/14.0	3	20/0	0.6	5.6	9.9	
11	1b	6	120	42.0/14.0	3	80/0	1.3	4.8	13.7	
12	1b	6	110	48.0/8.0	6	20/0	0.6	2.3	8.2	

^a Catalytic conditions: palladium, 0.012 mmol; P(total) at reaction temp., 56.0 bar; MeOH, 50 mL; stirring rate, 1300 rpm. ^b Productivity expressed as g(polyketone) (mmol(Pd) × h)⁻¹. ^c Determined by ¹H NMR spectra. ^d Total mol% of C₂H₄ involved in non-alternation, calculated from ¹³C{¹H} NMR spectra. ^e TFE, 50 mL.

of polyketones in fluorinated solvents, which improves the mass transfer.¹³

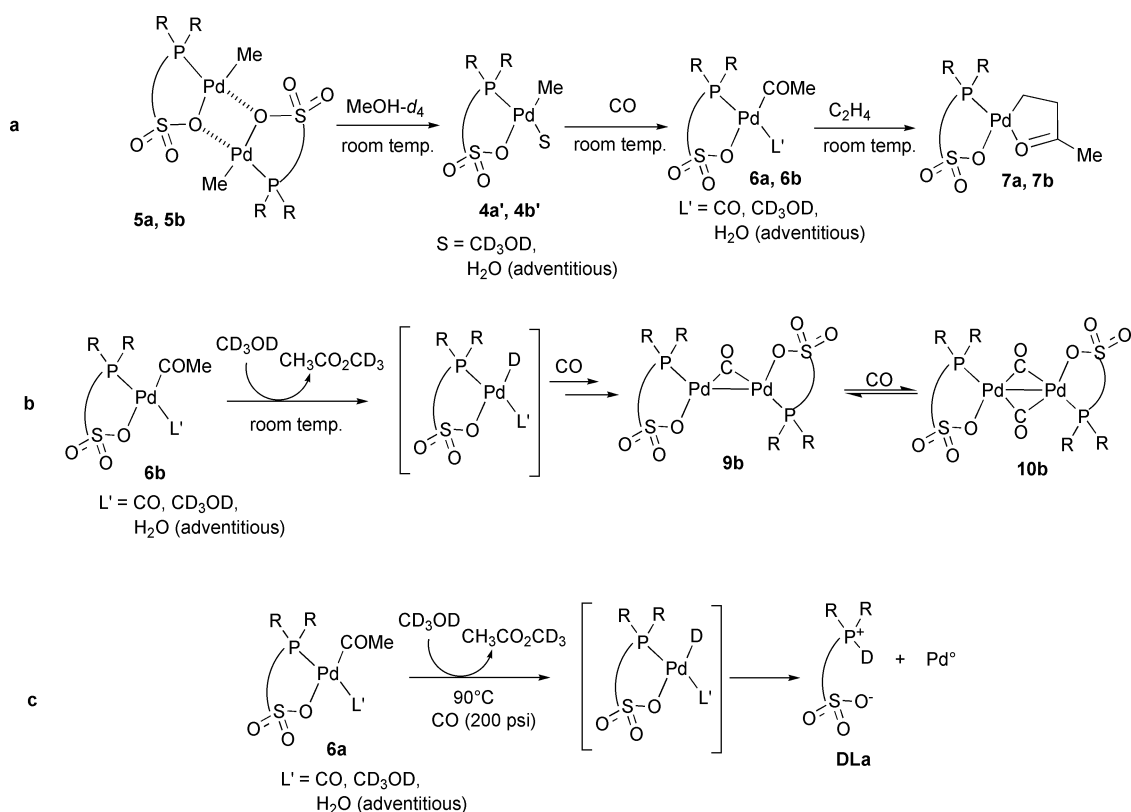
Model organometallic study

In an attempt to identify the organometallic species, which might form during the CO–C₂H₄ copolymerization reactions catalyzed by the present Pd^{II}(P ~ O) complexes in MeOH, the methyl derivatives **4a'** and **4b'** were employed as model compounds to study *in situ* the stepwise uptake of CO and ethylene. The results of this study are summarized in Scheme 5.

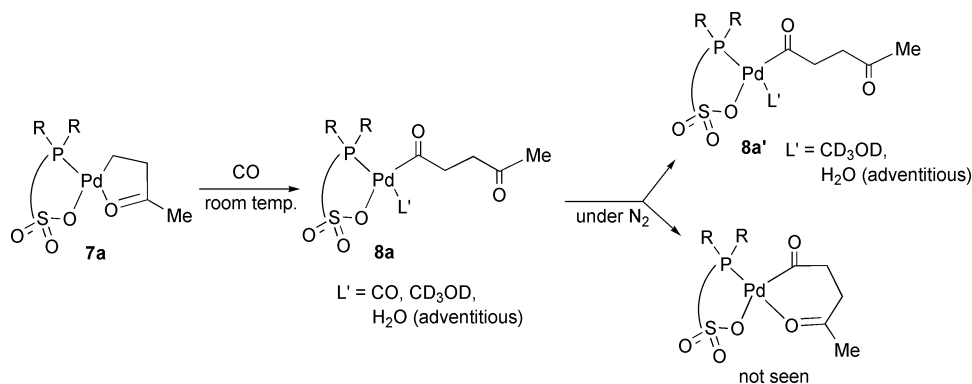
Bubbling CO into a NMR tube containing a MeOH-*d*₄ solution of either **4a'** or **4b'** at room temperature converted the latter compounds into the corresponding Pd^{II} acetyl complexes **6a** or **6b** (Scheme 5a). However, while the selective formation of **6a** occurred in 10 min, the complete disappearance of **4b'** required 40 min and, in addition to the acetyl complex **6b**, the two CO-bridged Pd^I dimers (μ-CO)[Pd(Lb)]₂ (**9b**) and [Pd(μ-CO)(Lb)]₂ (**10b**) were formed, showing a **6b** : **9b** : **10b** ratio of 2 : 1 : 1. The concomitant production of CH₃C(O)OCD₃ indicates that the formation of **9b** and **10b** proceeds *via* methanolysis of **6b** (Scheme 5b).¹⁴ The structure of the Pd(I) complexes **9b** and **10b** as shown in Scheme 5b have been assigned on the basis of the following considerations: (i) Both complexes are formed by the reaction of **6b** with methanol in the presence of CO. Therefore the formation of CO bridged Pd(I) complexes would be quite likely. (ii) The corresponding ¹H NMR spectrum exhibited no evidence for the formation of dimer Pd^I(μ-H)(μ-CO).¹⁵ (iii) The shift of the ³¹P NMR signal, from 23.66 ppm (**6b**) to 8.09 (**9b**) and 8.55 (**10b**) is characteristic for the formation of Pd^I species.¹⁵ (iv) Furthermore performing the methanolysis reaction of **6b** in the presence of *p*-benzoquinone (BQ) did not lead to the formation of **9b** and **10b**. The assignment of the ³¹P and ¹³C (carbonyl) NMR signals of both latter compounds was performed following the inter-conversion of compound **9b** into **10b** by bubbling CO through the corresponding MeOH-*d*₄ solution (Scheme 5b), while bubbling nitrogen through the same solution led to the conversion of **10b** into **9b**.

Unlike **6b**, the methanolysis reaction of **6a** required a much higher temperature to occur. Indeed, the process initiated at 90 °C yielding CH₃C(O)OCD₃, the deuterated free ligand **DLa** and palladium black (Scheme 5c).

The acetyl complexes **6a** and **6b** were characterized by ³¹P{¹H} and ¹³C{¹H} NMR spectroscopy. In either complex, the palladium(II) centre is square-planar coordinated by *cis* acetyl and phosphine groups with the fourth site presumably occupied by CD₃OD or adventitious water. In principle, one cannot disregard the existence of a fast exchange involving solvent molecules and CO, yet there is no proof for that. Indeed, the ³¹P{¹H} and ¹³C{¹H} NMR spectra of **6a**, **6b** are identical with those of the compounds obtained by removing CO from the reaction mixture. Moreover, the carbonylation of **4a'–4b'** with a (1 : 9) ¹³CO/¹²CO mixture (14.0 bar) showed no additional C–P coupling in the ¹³C{¹H} and ³¹P{¹H} NMR spectra as compared to those acquired under standard CO. The fact that CO forms stable species with Pd^I(P ~ O) fragments (compounds **9b** and **10b**, Scheme 5b) but not with Pd^{II}(P ~ O) fragments suggests that the Pd^{II} centre in the latter species is not sufficiently electron-rich for effective π-back bonding.



Scheme 5



Scheme 6

Bubbling ethylene into a $\text{MeOH-}d_4$ solution of **6a** for 2 min at room temperature led to the selective formation of the β -chelate **7a** (Scheme 5a). A longer ethylene bubbling time (20 min) was required to obtain the analogous complex **7b** from a 1 : 1 mixture of **6b** and **9b**. Under this condition the latter compound was stable. Compounds **7a** and **7b** showed NMR and the IR data (ν_{CO} at 1641 cm^{-1}), which are in line with *trans* P and $\text{O}_{\text{ keto}}$ donor atoms.

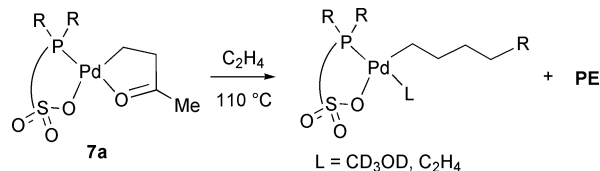
Complex **7a** was converted into the second-generation acyl complex $\text{Pd}(\text{L}')\text{COCH}_2\text{CH}_2\text{COMe}(\text{La})$ (**8a**) by bubbling CO into a $\text{MeOH-}d_4$ solution of **7a** at room temperature. A $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum acquired in $\text{MeOH-}d_4$ at room temperature under CO, showed a doublet at δ 221.44 with a $^2J_{\text{PC}}$ of 7.5 Hz and a singlet at 210.18, which can be assigned to the acyl group bonded to palladium and to the free COMe, respectively.^{7b} On the other hand, the NMR spectra did not allow us to determine whether L'

is CO, CD_3OD , or adventitious H_2O , eventually in fast exchange with each other. Indeed, replacing CO with N_2 for enough time to get rid of all dissolved CO gave a product (**8a'**) spectroscopically indistinguishable from **8a**, which confirms that the coordination of CO to $\text{Pd}^{\text{II}}(\text{P} \sim \text{O})$, if any, is dramatically weak (Scheme 6). As a matter of fact, the $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ of **8a** obtained using a 1 : 9 mixture of $^{13}\text{CO}/^{12}\text{CO}$ were identical to those acquired under non isotopically enriched CO.

In conclusion, this study has shown that neutral $\text{Pd}(\text{P} \sim \text{O})$ fragments are able to stabilise η^1 -acyl as well as β -chelate complexes under copolymerization conditions. Though no evidence of the formation of γ -chelates¹⁶ was obtained on the NMR timescale, the presence of such species in the catalysis cycle cannot be ruled out.

In an independent experiment, a HP NMR tube containing a $\text{MeOH-}d_4$ solution of **7a** was pressurized with 42.0 bar of ethylene.

Upon heating to 110 °C, linear polyethylene was formed, while the palladium precursor was most likely converted into a new species ($^{31}\text{P}\{^1\text{H}\}$ NMR δ 25.8) that we suggest to be an alkyl derivative (Scheme 7).



Scheme 7

Operando HP-NMR study

The model organometallic study described in the previous section has shown the formation and reactivity of several species that might be involved in the real catalytic cycle of the non-alternating CO–C₂H₄ copolymerization assisted by the present Pd(P ~ O) systems. In an attempt of discriminating purely model compounds from truly catalytic intermediates, at least those visible on the NMR timescale, *operando* HP-NMR experiments have been carried out with **5a** and **5b** at an overall 800 psi pressure using a 1 : 3 CO–C₂H₄ blend.

Since **5a** produces high molecular weight polyketones, the HP-NMR study with this precatalyst was performed in a 3 : 1 (v : v) mixture of TFE and C₆D₆ to favour as much homogeneous as possible conditions. The HP-NMR reaction catalyzed by **5b** was carried out in MeOH-*d*₄. A sequence of selected $^{31}\text{P}\{^1\text{H}\}$ NMR spectra are shown in Fig. 2 and 3.

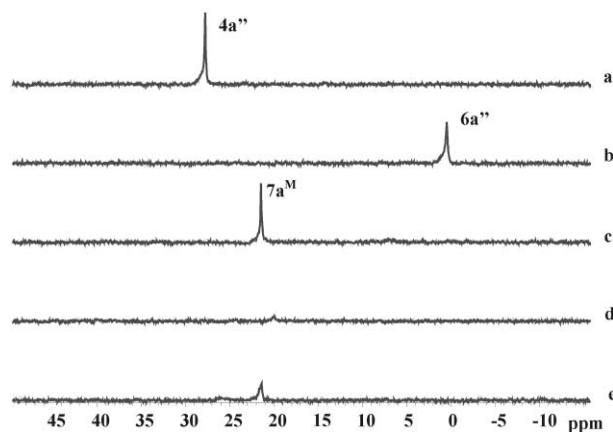


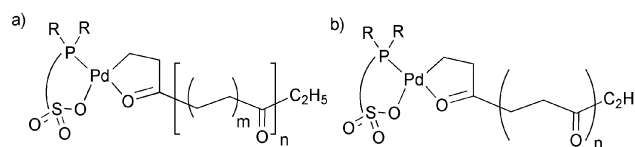
Fig. 2 Variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR study (sapphire tube, TFE/C₆D₆ (v : v) (3 : 1), 81.01 MHz) of the non-alternating CO–ethylene copolymerization reaction catalyzed by pre-catalyst **5a**: (a) **4a''** obtained from **5a** under nitrogen at 22 °C; (b) under CO (200 psi) at 22 °C; (c) under CO–C₂H₄ (1 : 3) (800 psi) at 22 °C; (d) after 10 min at 110 °C; (e) after cooling to 22 °C.

On dissolution in a 3 : 1 mixture of TFE/C₆D₆, **5a** converted immediately at room temperature into Pd(S)Me(La) (**4a''**; S = TFE or adventitious H₂O; Scheme 4) whose $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum consists of a singlet at δ 27.9 (Fig. 2, trace a). On pressurizing the sapphire tube with CO (14.0 bar) at room temperature, **4a''** was

completely converted into the acyl complex Pd(L')(COMe)(La) (**6a''** L' = CO, TFE or adventitious H₂O) (singlet at δ 0.20; Fig. 2, trace b). Replacing CO with a (1 : 9) $^{13}\text{C}/^{12}\text{C}$ mixture gave the same $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra with no evidence of CO coordination to palladium.

It is worth noticing that both the $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shift of **6a''** and the signal for the COCH₃ carbon atom (δ 211.49, $^2J_{\text{PC}}$ 3.9 Hz) in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6a''** are shifted in TFE/C₆D₆ as compared to the corresponding signals of **6a** in MeOH-*d*₄ ($^{31}\text{P}\{^1\text{H}\}$ NMR δ 13.60 (s); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 222.58, $^2J_{\text{PC}}$ 8.0 Hz). We are inclined to attribute this difference just to the presence of TFE that can form a network of hydrogen bonds involving oxygen atoms from metal complexes.^{7a,13} As a matter of fact, the addition of TFE to a MeOH-*d*₄ solution of **6a**, prepared as described above, caused a similar high field shift of the resonances.

Once compound **6a''** was formed, the sapphire tube was pressurized with 600 psi of ethylene at room temperature. As a result, the acyl complex was completely transformed into the β -chelate species **7a^M**, which is most likely a mixture of different generations of such compounds due to subsequent insertions of CO and C₂H₄. These β -chelates are featured by a $^{31}\text{P}\{^1\text{H}\}$ NMR singlet at δ 21.50 (Fig. 2, trace c), almost in the same position of the first generation β -chelate **7a** (δ 21.73). Apparently, the steric congestion caused by the growing polyketone chain does not allow TFE to affect significantly the environment of the P–Pd moiety. Heating the NMR tube to 110 °C (Fig. 2, trace d) and then cooling it down to room temperature (Fig. 2, trace e) did not form other NMR-detectable species than the β -chelates **7a^M**. The broader NMR signal observed after catalysis is attributed to the formation of further generations of β -chelates with different propagating tails (Scheme 8a). Consistently, non-alternating polyketones were collected from the NMR tube after this was heated for 1 h at 110 °C.



Scheme 8

The fact that the copolymerization catalyzed by **5a** initiates already at room temperature is remarkable as it has allowed us to collect enough material to establish its prevalent perfectly alternating structure (< 1.0% of extra-ethylene inserted) (separate experiment lasting 12 h) (Scheme 8b).

An analogous variable-temperature HP-NMR experiment was carried out using pre-catalyst **5b** in MeOH-*d*₄ (Fig. 3). At room temperature, the spectrum showed a singlet at δ 38.00 due to **4b'** (Fig. 3, trace a). On pressurizing the tube with 14.0 bar of CO, **4b'** was immediately converted into a mixture of the acyl **6b** (largely prevailing) and of the binuclear Pd^I complex **10b**, formed by methanolysis of **6b** (Scheme 5). The addition of 600 psi of ethylene converted **6b** into the β -chelates **7b^M** already at room temperature. Upon heating the tube to 110 °C, the complete conversion of **6b** and **10b** into **7b^M** occurred within a few minutes (Fig. 3, trace d), which means that the μ -CO Pd^I dimer is not a dead end for the CO–C₂H₄ copolymerization reaction.^{14b} The β -chelates **7b^M** were the only phosphorus-containing compounds also at room

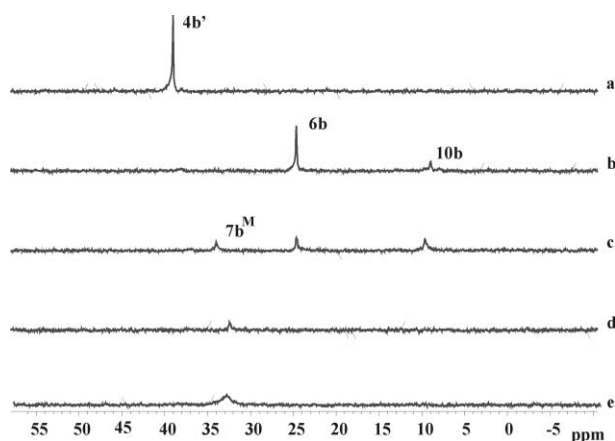


Fig. 3 Variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR study (sapphire tube, $\text{MeOH-}d_4$, 81.01 MHz) of the non-alternating CO–ethylene copolymerization reaction catalyzed by pre-catalyst **5b**: (a) **4b'** obtained from **5b** under nitrogen at 22 °C; (b) under CO (200 psi) at 22 °C; (c) under CO– C_2H_4 (1 : 3) (800 psi) at 22 °C; (d) after 10 min at 110 °C; (e) after cooling to 22 °C.

temperature (Fig. 3, trace e). Again, the broadness of the resonance is attributed to the formation of several generations of β -chelates.

The $^{31}\text{P}\{^1\text{H}\}$ HPNMR experiment illustrated in Fig. 3 was repeated in the presence of TsOH (20 equiv.) added just after dissolving **5b** in $\text{MeOH-}d_4$. Since the NMR picture was fully comparable to that shown in Fig. 2, one may conclude that also in effective copolymerization conditions (Table 4), the β -chelates are key intermediates in the catalysis cycle.

Mechanistic considerations

The model organometallic and *operando* studies have shown that the two $\text{Pd}^{\text{II}}(\text{P} \sim \text{O})$ systems under investigation catalyze the non-alternating CO– C_2H_4 copolymerization *via* quite similar mechanisms. For catalytic systems exhibiting both a similar mechanism and a comparable chemical stability, a dramatically different activity, as it has been observed for **1a** and **1b**, would be interpreted in terms of different rates of relevant steps in the catalytic cycle. Unfortunately, both precursors and intermediates supported by **Lb** are much less stable than analogous derivatives supported by **La**. Therefore, it is very likely that the main reason for the much lower productivity of the reactions catalyzed by **1b** is just the faster degradation of catalytically active species into inactive ones. Since **La** and **Lb** differ only for the backbone rigidity of the spacer between the $\text{P}(\text{aryl})_2$ and SO_3^- groups, one may suggest that the more flexible ligand **Lb**, having a higher degree of freedom, does not chelate the metal centre as strongly as **La**, leading to less stable monodentate complexes, which may be favoured on increasing the amount of Brønsted-acid. The positive effect of ligand rigidity in catalysis has innumerable precedents in the literature, including several examples of CO–olefin copolymerization.¹⁷

Keeping in mind that the lower productivity of the reactions assisted by **1b** and related species is mainly due to the lower catalyst stability, let us proceed to analyze the results obtained in the course of the model and *operando* studies. Indeed, we feel that some of these results are very useful to better comprehend the different activity of the catalysts investigated, while others may contribute

to elucidate the intrinsic factors that, in a broader sense, favour non-alternation over perfect alternation.

Two clear facts have emerged from the carbonylation of $\text{Pd}^{\text{II}}(\text{P} \sim \text{O})$ alkyl precursors: (i) The formation of acyl complexes (migratory insertion of $\text{Pd}(\text{alkyl})\text{CO}$) is much faster for the species supported by **La** (Scheme 5), but neither system forms stable CO adducts (Schemes 5 and 6). The latter evidence contrasts remarkably with the behaviour of $\text{Pd}^{\text{II}}(\text{diphosphine})$ catalysts for the perfect CO– C_2H_4 alternation that invariably form detectable $\text{Pd}(\text{acyl})\text{CO}$ or $\text{Pd}(\text{alkyl})\text{CO}$ intermediates with relevance in the rate-determining step.^{1,7b,16c} As suggested in a previous section, the low propensity to bind strongly CO, as a crucial factor for favouring multiple ethylene insertions,^{3d,e} may be due to the scarce basicity of the Pd^{II} centres modified with $\text{P} \sim \text{O}^-$ ligands. (ii) Once formed, the acyl complexes exhibit different reactivity with methanol: the complex with **La** is stable at room temperature and undergoes methanolysis only at 90 °C; in contrast, the acyl complex with ligand **Lb** reacts with MeOH already at room temperature. Since methanolysis is an effective chain transfer mechanism in the present copolymerization reactions, this evidence may account for the lower activity and smaller molecular weight materials obtained with **1b**.

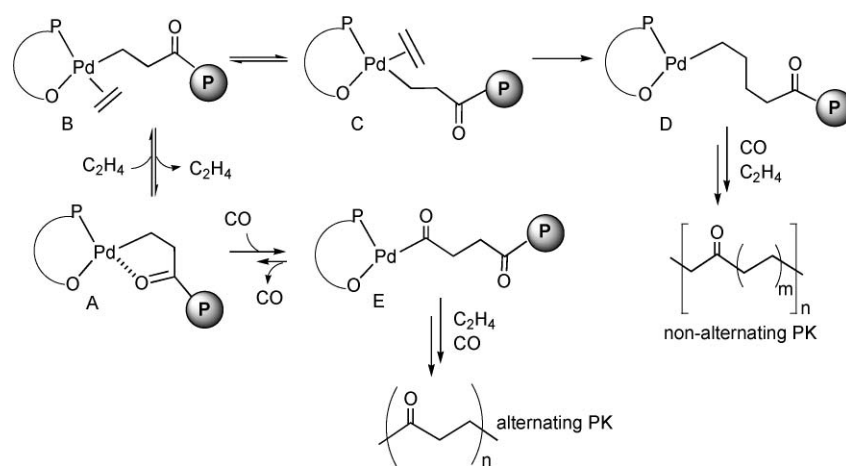
Convincing evidence has been accumulated showing β -chelates to be key intermediates in the non-alternating copolymerization (Figs. 2 and 3) as hypothesized by Drent.^{3a} In particular, the formation of both β -chelates (migratory insertion of $\text{Pd}(\text{acyl})\text{C}_2\text{H}_4$) is much faster for the species supported by **La** (Scheme 5a). Unlike the β -chelates supported by diphosphine ligands and selective for perfect alternation, however, the β -chelates supported by the $\text{P} \sim \text{O}^-$ ligands are opened to the alkyl form *both by CO and by ethylene* (Schemes 6 and 7), which contrasts with the behaviour of $\text{Pd}^{\text{II}}(\text{diphosphine})$ analogues opened exclusively by CO.^{16b}

Theoretical studies of the non-alternating CO–ethylene copolymerization catalyzed by neutral $\text{Pd}(\text{P} \sim \text{O})$ complexes suggest that the rate determining step for the extra-ethylene insertion is the migratory insertion of $\text{Pd}(\text{alkyl})(\text{C}_2\text{H}_4)$ (intermediate C) shown in Scheme 9.^{3d,e} This scheme has been supplemented with the introduction of a β -chelate intermediate.

Therefore, the experimental conditions that favour the accumulation of intermediate C at the expense of the concentration of intermediate E would favour the extra-ethylene insertion into the growing polymeric chain.^{3d,e} Indeed, the extra-ethylene insertion increases by increasing the partial pressure of ethylene and the reaction temperature.³ Furthermore the increasing amount of Brønsted acid in combination with the more flexible precatalysts **1b/5b** may favour the unfastening of the sulfonate unit from the palladium atom thus favouring the isomerization reaction of the $\text{Pd}(\text{alkyl})(\text{C}_2\text{H}_4)$ species B into C. Indeed, from theoretical calculations emerged, that the latter species inserts ethylene much more rapidly than the former one does, due to the fact, that the phosphorus atom in species C exerts a higher *trans* influence on the migrating alkyl group as compared to the oxygen atom in species B.^{3d,e}

Conclusions

A comparative study of the non-alternating CO– C_2H_4 copolymerization reaction catalyzed by neutral Pd^{II} complexes modified with phosphine–sulfonate ligands has shown that the higher the



Scheme 9

backbone rigidity of the $P \sim O$ ligand, the higher the catalytic activity, the molecular weight and the extra-ethylene contents of the polyketones.

Operando HP-NMR studies have allowed us to intercept for the first time Pd^{II} (phosphine–sulfonate) β -chelates in the catalysis cycle, while model organometallic reactions have contributed to demonstrate that $Pd^{II}(P \sim O)$ fragments do not form stable carbonyl complexes. Notably, the opening of $Pd^{II}(P \sim O)$ β -chelates is a viable process by either comonomer, which contrasts with the behaviour of Pd^{II} (diphosphine) catalysts for the perfectly alternating copolymerization. This finding may be the clue to rationalize the mechanism of the non-alternating $CO-C_2H_4$ copolymerization as well as design improved catalytic systems for such a process.

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 or Fluka, unless stated otherwise. $(2-MeO-C_6H_4)_2P(H)C_6H_4SO_3^{3a}$ (**HLA**), $(2-MeO-C_6H_4)_2P(H)C_2H_4SO_3^{3b}$ (**HLb**), $PdCl(Me)(cod)$ ($cod = 1,5$ -cyclooctadiene),¹⁸ $[Pd(\mu-Cl)(\eta^1, \eta^2-codyl^*)]_2$ ($codyl^* = 2$ -methoxycyclooct-5-enyl),⁵ $Pd(\eta^1, \eta^2-codyl^*)(Lb)^4$ (**1b**), and $[PdClMe(La)](NH_4Et_3)^8$ (**3a**) were prepared according to literature methods. All the isolated solid samples were collected on sintered-glass frits and washed with appropriate solvents before being dried under a stream of nitrogen. Copolymerization reactions were performed with a 200 mL stainless steel autoclave constructed at the ICCOM-CNR, equipped with a magnetic drive stirrer and a temperature and pressure controller. The autoclave was connected to a gas reservoir to maintain a constant pressure during the catalytic reactions. GC-MS analyses of the solutions were performed on a Shimadzu QP2010S apparatus equipped with a SPB-1 Supelco fused silica capillary column (30 m, 0.25 mm i.d., 0.25 μ m film thickness). Deuterated solvents for routine NMR measurements were dried over molecular sieves. 1H , $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR spectra were obtained on either a

Bruker ACP 200 (200.13, 50.32 and 81.01 MHz, respectively) or a Bruker Avance DRX-400 spectrometer (400.13, 100.62 and 161.98 MHz), respectively. Chemical shifts are reported in ppm (δ) relative to TMS, referenced to the chemical shifts of residual solvents resonances (1H and ^{13}C NMR) or 85% H_3PO_4 (^{31}P NMR). High-pressure NMR (HP-NMR) experiments were carried out on a Bruker ACP 200 using a 10 mm HP-NMR tube (Saphikon sapphire tube purchased from Milford, NH; titanium high-pressure charging head constructed at the ICCOM-CNR).¹⁹ Elemental analyses were performed using a Carlo Erba Model 1106 elemental analyzer. Infrared spectra were recorded on a FT-IR Spectrum GX instrument (Perkin Elmer). Polyketone products were analysed by IR, 1H , and $^{13}C\{^1H\}$ NMR spectroscopy. The NMR measurements were performed in a solvent mixture of 1,1,1,3,3,3-hexafluoroisopropanol- d_2 (HFIP- d_2)/ C_6D_6 (1 : 3, v/v). The assignment of $^1H^9$ and $^{13}C\{^1H\}$ NMR^{3a} chemical shifts was made on the basis of reports in the literature. The number-average molecular weight (M_n) of the low-molecular weight copolymers was determined by 1H NMR spectroscopy. The extra C_2H_4 insertion (%) was calculated from $^{13}C\{^1H\}$ NMR spectra. Melting points were recorded on a Stuart Scientific SMP3 apparatus.

Preparations

$Pd(\eta^1, \eta^2-codyl^*)(La)$ (1a**).** A solution of $[Pd(\mu-Cl)(\eta^1, \eta^2-codyl^*)]_2$ (103.4 mg, 0.184 mmol) in CH_2Cl_2 (2 mL) was added to a solution of the sodium salt of the ligand previously prepared *in situ* by reaction of NaH (14.7 mg, 0.368 mmol) with **HLA** (148.2 mg, 0.368 mmol) in CH_2Cl_2 (5 mL) for 30 min at room temperature. After 1 h stirring at room temperature, the resulting solution was concentrated to 2 mL. Addition of *n*-pentane (10 mL) led to the precipitation of a yellow microcrystalline product, which was filtered off and washed with *n*-pentane. Yield 67% (160 mg). $C_{29}H_{33}O_6PPdS$ (647.03): calc. C 53.83, H 5.14; found C 53.42, H 5.01%. 1H NMR ($CDCl_3$, 400.13 MHz): δ 1.70–2.72 (m, 10H, $codyl-H$), 2.42 (s, 3H, $codyl-OMe$), 3.59 (s, 3H, $Ar-OMe$), 3.65 (s, 3H, $Ar-OMe$), 6.04 (m, 1H, $codyl-H$), 6.72 (m, 1H, $codyl-H$), 6.92–7.51 (m, 10H, $Ar-H/Anisyl-H$), 8.07 (dd, $^3J(HP)$ 20.0 Hz, $^3J(HH)$ 8.0 Hz, 1H, $Ar-H_o$), 8.16 (dd, $^3J(HP)$ 12.4 Hz, $^3J(HH)$ 10.0 Hz, 1H, $Anisyl-H_o$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.62 MHz): δ 25.37 (s, $codyl-C$), 28.62 (s, $codyl-C$), 30.72 (s, $codyl-C$), 35.26

(s, codyl-C), 40.72 (s, codyl-C), 54.82 (s, OMe), 55.27 (s, OMe), 55.54 (s, OMe), 81.55 (s, codyl-C), 111.24 (s, Ar-C), 114.70 (d, $^1J(\text{CP})$ 52.0 Hz, Ar-C_{ipso}), 115.37 (d, $^1J(\text{CP})$ 52.0 Hz, Ar-C_{ipso}), 117.08 (d, $^3J(\text{CP})$ 9.2 Hz, CH), 120.85 (d, $^3J(\text{CP})$ 9.4 Hz, Ar-C), 121.14 (d, $^3J(\text{CP})$ Ar-C), 121.42 (d, $^2J(\text{CP})$ 12.1 Hz, CH), 127.10 (d, $^1J(\text{CP})$ 51.5 Hz, Ar-C_{ipso}), 127.85 (d, $^2J(\text{CP})$ 7.5 Hz, Ar-C), 128.45 (d, $^2J(\text{CP})$ 6.8 Hz, Ar-C), 130.27 (s, Ar-C), 132.93 (s, Ar-C), 134.27 (s, Ar-C), 134.90 (s, Ar-C), 134.93 (d, $^3J(\text{CP})$ 5.2 Hz, Ar-C), 140.47 (d, $^2J(\text{CP})$ 27.8 Hz, Ar-C), 147.90 (s, Ar-C), 160.04 (s, Ar-C), 161.06 (s, Ar-C). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 161.98 MHz): δ 8.20 (s).

Thermal reaction of 1a in MeOH: synthesis of Pd(La)₂ (2a). Compound **1a** (84.1 mg, 0.13 mmol) was dissolved in MeOH (3 mL) under nitrogen and heated to 90 °C for 2 h. During this time yellow microcrystals of **2a** precipitated along with palladium black. The solution was allowed to cool slowly to room temperature. The product was decanted, filtered and washed with *n*-pentane (3 mL). The product was insoluble in common organic solvents including DMF and DMSO. Yield: 40% (23.6 mg). $\text{C}_{40}\text{H}_{36}\text{O}_{10}\text{P}_2\text{PdS}_2$ (908.83): calc. C 52.86, H 3.96; found C 52.99, H 4.52%.

Thermal reaction of 1b in MeOH: synthesis of Pd(Lb)₂ (2b). Compound **1b** (80.0 mg, 0.13 mmol) was dissolved in MeOH (3 mL) under nitrogen and heated to 60 °C for 30 min. During this time yellow microcrystals of **2b** precipitated along with palladium black. The solution was allowed to cool slowly to room temperature. The product was decanted, filtered and washed with *n*-pentane (3 mL). The product was insoluble in common organic solvents including DMF and DMSO. Yield: 36% (19.0 mg). $\text{C}_{32}\text{H}_{36}\text{O}_{10}\text{P}_2\text{PdS}_2$ (813.12): calc. C 47.27, H 4.46; found C 47.01, H 4.38%.

Alternative synthesis of 2b. A solid sample of the ligand **HLb** (38.5 mg, 0.109 mmol) was added to a solution of Pd(OAc)₂ (12.2 mg, 0.054 mmol) in CH_2Cl_2 (2 mL). The resulting solution was allowed to stand for 3 h at room temperature. During this time the product precipitated as yellow crystals, which were filtered off and washed with diethyl ether (5 mL). Yield: 65% (28 mg). $\text{C}_{32}\text{H}_{36}\text{O}_{10}\text{P}_2\text{PdS}_2$ (813.12): calc. C 47.27, H 4.46; found C 46.95, H 4.45%.

[PdClMe(Lb)](NHET₃) (3b). Triethylamine (97.6 μL , 0.70 mmol) was syringed into a solution of ligand **HLb** (49.6 mg, 0.14 mmol) in CH_2Cl_2 (10 mL). After 15 min stirring at room temperature, solid PdClMe(cod) (37.1 mg, 0.14 mmol) was added. The resulting solution was stirred for 1 h at room temperature and then filtered through a Celite column. Addition of *n*-hexane (20 mL) caused the precipitation of the product as off-white microcrystals, which were filtered off and washed with *n*-hexane. Yield: 73% (62 mg). $\text{C}_{23}\text{H}_{37}\text{ClNO}_5\text{PdPS}$ (612.46): calc. C 45.11, H 6.09; found C 45.01, H 5.97%. ^1H NMR ($\text{MeOH}-d_4$, 400.13 MHz): δ 0.37 (s, 3H, PdMe), 1.33 (t, $^3J(\text{HH})$ 7.2 Hz, 9H, CH_2CH_3), 3.02 (m, 2H, CH_2S), 3.12 (m, 2H, CH_2P), 3.22 (q, $^3J(\text{HH})$ 7.2 Hz, 6H, NCH_2), 3.91 (s, 6H, OMe), 7.05 (m, 2H, Ar-H), 7.15 (m, 2H, Ar-H), 7.57 (m, 2H, Ar-H), 7.68 (m, 2H, Ar-H). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{MeOH}-d_4$, 100.62 MHz): δ -0.20 (s, 1C, PdMe), 7.87 (s, 3C, CH_2CH_3), 22.32 (d, $^1J(\text{CP})$ 33.7 Hz, 1C, CH_2P), 46.48 (s, 3C, CH_2CH_3), 47.60 (overlapped signal, 1C, CH_2S), 55.12 (s, 2C, OMe), 111.31 (d, $^3J(\text{CP})$ 4.3 Hz, 2C,

Ar- CH_m), 111.59 (d, $^1J(\text{CP})$ 53.7 Hz, 2C, Ar-C_{ipso}), 120.55 (d, $^3J(\text{CP})$ 11.2 Hz, 2C, Ar- CH_o), 133.25 (s, 2C, Ar- CH_o), 135.81 (s, 2C, Ar- CH_p), 160.62 (s, 2C, Ar-C_o). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{MeOH}-d_4$, 161.98 MHz): δ 31.44 (s).

Reaction of [PdClMe(L)](NHET₃) (L = La (3a), Lb (3b)) with AgOTs: *in situ* synthesis of neutral complexes of the type Pd(solvent)Me(L). The appropriate chloro-methylpalladium complex (0.12 mmol) was added to a Schlenk flask containing a solution of AgOTs (OTs = *p*-toluenesulfonate, 33.5 mg, 0.12 mmol) in CD_2Cl_2 (2 mL) at room temperature. After 20 min stirring, the solution was carefully filtered and introduced by a syringe into a NMR tube. Multinuclear NMR analysis showed the formation of (NHET₃)OTs together with a new methylpalladium complex of the formula Pd(S)Me(L) (S = CD_2Cl_2 or adventitious water).¹⁰ Spectroscopic data of Pd(S)Me(La). ^1H NMR (CD_2Cl_2 , 400.13 MHz): δ 0.16 (s, 3H, PdMe), 3.69 (s, 6H, OMe), 7.05–7.61 (m, 11H, Ar-H), 8.04 (dd, $^3J(\text{HH})$ 7.5 Hz, $^4J(\text{HP})$ 4.6 Hz, 1H, Ar-H_o). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 161.98 MHz): δ 26.90 (s). Spectroscopic data of Pd(S)Me(Lb). ^1H NMR (CD_2Cl_2 , 400.13 MHz): δ 0.31 (s, 3H, PdMe), 3.1–3.3 (m, 4H, CH_2CH_2), 3.91 (s, 6H, OMe), 7.0–7.8 (m, 8H, Ar-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 161.98 MHz): δ 37.61 (s). After the extraction of (NHET₃)OTs with D₂O, the NMR spectra of the residual CD_2Cl_2 solution showed no significant change, which is consistent with the presence of the same methylpalladium complex, most likely as a D₂O adduct (*vide infra*, **4a,4b**). Evaporation under reduced pressure of this CD_2Cl_2 solution led to an off-white solid residue (**5a,5b**, *vide infra*) that, once formed, was completely insoluble in CD_2Cl_2 , whereas it dissolved readily in $\text{MeOH}-d_4$. The NMR spectra of these solutions were practically identical to those of the solvated methylpalladium complexes reported above. Accordingly, we think that the coordinated solvent is either $\text{MeOH}-d_4$ or water (*vide infra*, **4a'–4b'**) with a preference for the latter as reported in the literature for Pd^{II} complexes with chelating ligands.¹⁰

Synthesis of [PdMe(L)]₂ (L = La (5a), Lb (5b)). The appropriate chloro-methylpalladium complex **3a,3b** (0.20 mmol) was added to a Schlenk flask containing a solution of AgOTs (0.21 mmol) in CD_2Cl_2 (5 mL) at room temperature. The suspension was stirred for 30 min and then filtered through a Celite column. The CH_2Cl_2 solution was extracted with water (3 \times 5 mL). Solvent evaporation under reduced pressure led to an off-white solid residue of the dinuclear complex **5a,5b** in rather low yield: **5a**, 36.0 mg (35%); **5b**, 38.0 mg (40%). $\text{C}_{42}\text{H}_{42}\text{O}_{10}\text{Pd}_2\text{P}_2\text{S}_2$ (1045.70) (**5a**): calc. C 48.24, H 4.05; found C 48.15, H 3.90%. $\text{C}_{34}\text{H}_{42}\text{O}_{10}\text{Pd}_2\text{P}_2\text{S}_2$ (949.61) (**5b**): C 43.00, H 4.46; found C 42.91, H, 4.37%. Both dinuclear complexes were not soluble in CH_2Cl_2 but very soluble in MeOH (or $\text{MeOH}-d_4$) where they regenerated the mononuclear complexes Pd(S)Me(L) (L = La (**4a'**), Lb (**4b'**); S = $\text{MeOH}/\text{MeOH}-d_4$ and/or adventitious H₂O). Spectroscopic data for **4a'**. ^1H NMR ($\text{MeOH}-d_4$, 400.13 MHz): δ 0.18 (d, $^3J(\text{HP})$ 0.8 Hz, 3H, PdMe), 3.69 (s, 6H, OMe), 7.05–7.61 (m, 11H, Ar-H), 8.02 (dd, $^3J(\text{HH})$ 7.6 Hz, $^4J(\text{HP})$ 4.8 Hz, 1H, Ar-H_o). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{MeOH}-d_4$, 100.62 MHz): δ -0.63 (s, PdMe), 54.31 (s, OMe), 111.33 (d, $^3J(\text{CP})$ 4.3 Hz, Ar- CH_m), 115.37 (d, $^1J(\text{CP})$ 61.4 Hz, Ar-C_{ipso}), 120.20 (d, $^3J(\text{CP})$ 12.5 Hz, Ar- CH_m), 126.80 (d, $^3J(\text{CP})$ 8.3 Hz, Ar-CH), 127.84 (d, $^1J(\text{CP})$ 53.0 Hz, Ar-C_{ipso}), 128.74 (d, $^3J(\text{CP})$ 8.2 Hz, Ar-CH), 129.99 (s, 2C, Ar-CH), 133.56 (s, Ar-CH_o), 134.92 (s, Ar-CH), 137.40 (s, Ar-CH_p), 146.87 (d, $^2J(\text{CP})$ 14.0 Hz, Ar-

C), 160.44 (s, Ar-C_o). ³¹P{¹H} NMR (MeOH-*d*₄, 161.98 MHz): δ 26.98 (s). Spectroscopic data for **4b'**. ¹H NMR (MeOH-*d*₄, 400.13 MHz): δ 0.11 (d, ³J(HP) 1.2 Hz, 3H, PdMe), 3.06 (m, 2H, CH₂S), 3.12 (m, 2H, CH₂P), 3.90 (s, 6H, OMe), 7.04–7.65 (m, 8H, Ar-H). ¹³C{¹H} NMR (MeOH-*d*₄, 100.62 MHz): δ -2.22 (s, PdMe), 22.99 (d, ¹J(CP) 35.2 Hz, CH₂P), 46.84 (s, CH₂S), 54.78 (s, OMe), 111.31 (d, ³J(CP) 4.3 Hz, Ar-CH_m), 115.32 (d, ¹J(CP) 53.7 Hz, Ar-C_{ipso}), 120.55 (d, ³J(CP) 11.2 Hz, Ar-CH_m), 133.25 (s, Ar-CH_o), 136.91 (s, Ar-CH_p); 160.36 (s, Ar-C_o). ³¹P{¹H} NMR (MeOH-*d*₄, 161.98 MHz): δ 37.67 (s). The low yields of **5a** and **5b** were simply due to the extraction procedure adopted. Indeed, on concentrating the water phases to dryness, a solid residue was obtained, which was dissolved in MeOH-*d*₄ and authenticated by NMR spectroscopy as a mixture of (NHET₃)OTs and either **4a'** or **4b'**.

Reaction of 4a'–4b' with CO: *in situ* synthesis of Pd(L')-(COMe)(L) (L = La (6a), Lb (6b); L' = CO, CD₃OD, H₂O). A sample of **5a,5b** (0.05 mmol) was dissolved in MeOH-*d*₄ (1.5 mL) and the solution was transferred into a 5 mm NMR tube. The NMR spectra of this solution showed the presence of the mononuclear methylpalladium complex **4a',4b'**. Bubbling CO through a solution of **4b'** at room temperature converted the latter compound into a 2 : 1 : 1 mixture of **6b** and the CO-bridged Pd^I dimers (μ-CO)[Pd(Lb)]₂ (**9b**) and [Pd(μ-CO)(Lb)]₂ (**10b**) in 40 min. The formation of the latter two complexes was preceded by the methanolysis of **6b** as indicated by the production of CH₃C(O)OCD₃ (¹H NMR and GC/MS analysis). Bubbling nitrogen through the final reaction mixture converted **10b** into **9b**, which accounted for the assigned structures. In contrast, bubbling CO through the solution of **4a'** at room temperature produced quantitatively the acetyl complex **6a** in only 10 min. To verify an eventual methanolysis reaction of **6a**, the corresponding MeOH-*d*₄ solution contained in a 10 mm HPNMR tube was progressively heated under CO (14.0 bar). At 90 °C, the methanolysis reaction occurred yielding CH₃C(O)OCD₃ and the deuterated free ligand **DLa** in its zwitterionic form. Selected spectroscopic data for **DLa**. ³¹P{¹H} NMR (MeOH-*d*₄, 90 °C, 81.01 MHz): δ -9.20 (br. s). ³¹P{¹H} NMR (CD₂Cl₂, 90 °C, 81.01 MHz): δ -10.80 (1 : 1 : 1 triplet, ¹J(PD) 92.0 Hz). When the solutions of **6a** or **6b** (**9b/10b**) were treated with nitrogen to eliminate the excess of CO, no change in their ¹³C{¹H} and ³¹P{¹H} NMR spectra of **6a,6b** was observed. The carbonylation reactions of **4a',4b'** were carried out also under a (1 : 9) ¹³CO/¹²CO mixture (14.0 bar): no additional C–P coupling was detected in the ¹³C{¹H} and ³¹P{¹H} NMR spectra as compared to those acquired under standard CO. These additional experimental evidences indicated that, under CO atmosphere, the fourth position in the palladium coordination sphere of both acetyl complexes was occupied by CO and solvent molecules in rapid exchange. Selected spectroscopic data for **6a**. ¹H NMR (MeOH-*d*₄, 400.13 MHz): δ 1.85 (d, ⁴J(HP) 0.4 Hz, 3H, COMe). ¹³C{¹H} NMR (MeOH-*d*₄, 100.62 MHz): δ 34.24 (d, ³J(CP) 29.2 Hz, COMe), 222.58 (d, ²J(CP) 8.0 Hz, COMe). ³¹P{¹H} NMR (MeOH-*d*₄, 161.98 MHz): δ 13.60 (s). Selected spectroscopic data for **6b**. ¹H NMR (MeOH-*d*₄, 400.13 MHz): δ 1.84 (d, ⁴J(HP) 0.4 Hz, 3H, COMe). ¹³C{¹H} NMR (MeOH-*d*₄, 100.62 MHz): δ 32.38 (d, ³J(CP) 28.1 Hz, COMe), 223.34 (s, COMe). ³¹P{¹H} NMR (MeOH-*d*₄, 161.98 MHz): δ 23.66 (s). Selected spectroscopic data for **9b**. ¹³C{¹H} NMR (MeOH-

*d*₄, 100.62 MHz): δ 227.60 (s, CO). ³¹P{¹H} NMR (MeOH-*d*₄, 161.98 MHz): δ 8.09 (s). Selected spectroscopic data for **10b**. ¹³C{¹H} NMR (MeOH-*d*₄, 100.62 MHz): δ 225.36 (s, CO). ³¹P{¹H} NMR (MeOH-*d*₄, 161.98 MHz): δ 8.55 (s).

Reaction of 6a,6b with C₂H₄: *in situ* synthesis of PdCH₂CH₂-COMe(L) (L = La, 7a; Lb, 7b). A MeOH-*d*₄ solution of **6a,6b** (**9b/10b**) prepared as reported above at room temperature was treated with nitrogen for 2 min to eliminate the excess CO. During this procedure **10b** converted into **9b**. Bubbling ethylene at room temperature for 2 and 20 min, respectively, led to the complete transformation of **6a,6b** into **7a,7b**. IR spectroscopic data in CH₂Cl₂ for **7a** and **7b** were obtained by evaporating both MeOH-*d*₄ solutions to dryness and re-dissolving the residue in CH₂Cl₂. Selected spectroscopic data for **7a**. ¹H NMR (MeOH-*d*₄, 400.13 MHz): δ 1.33 (td, ³J(HH) 6.2 Hz, ³J(HP) 2.6 Hz, 2H, PdCH₂), 2.36 (s, 3H, COMe), 2.84 (t, ³J(HH) 6.2 Hz, 2H, COCH₂). ¹³C{¹H} NMR (MeOH-*d*₄, 100.62 MHz): δ 20.63 (s, PdCH₂), 26.34 (s, COMe), 49.80 (s, COCH₂), 231.59 (s, COMe). ³¹P{¹H} NMR (MeOH-*d*₄, 161.98 MHz): δ 21.73 (s). IR (CH₂Cl₂): ν(CO) 1641 cm⁻¹. Selected spectroscopic data for **7b**. ¹H NMR (MeOH-*d*₄, 400.13 MHz): δ 1.21 (td, ³J(HH) 6.2 Hz, ³J(HP) 2.4 Hz, 2H, PdCH₂), 2.30 (s, 3H, COMe), 2.81 (t, ³J(HH) 6.2 Hz, 2H, COCH₂). ¹³C{¹H} NMR (MeOH-*d*₄, 100.62 MHz): δ 19.80 (s, PdCH₂), 26.02 (s, COMe), 49.47 (s, COCH₂), 230.86 (s, COMe); ³¹P{¹H} NMR (MeOH-*d*₄, 161.98 MHz): δ 32.80 (s). IR (CH₂Cl₂): ν(CO) 1641 cm⁻¹.

Reaction of 7a with CO: *in situ* synthesis of Pd(L')COCH₂-CH₂COMe(La) (8a; L' = CO, CD₃OD, H₂O). A MeOH-*d*₄ solution of **7a** prepared as reported above at room temperature was treated with nitrogen for 2 min to eliminate the excess ethylene. Bubbling CO at room temperature for 10 min led to the complete transformation of **7a** into **8a**. Bubbling nitrogen through the solution of **8a** caused no change in the ¹³C{¹H} and ³¹P{¹H} NMR spectra. To verify the eventual coordination of CO in **8a**, the reaction was carried out also under a (1 : 9) ¹³CO/¹²CO mixture (14.0 bar): no additional C–P coupling was detected in the ¹³C{¹H} and ³¹P{¹H} NMR spectra, which confirmed that the fourth position in the palladium coordination sphere was occupied by CO and solvent molecules in rapid exchange. Selected spectroscopic data for **8a**. ¹H NMR (MeOH-*d*₄, 400.13 MHz): δ 2.02 (s, 3H, COMe), 2.18 (t, ³J(HH) 6.6 Hz, 2H, CH₂CO), 2.61 (t, ³J(HH) 6.6 Hz, 2H, PdCOCH₂). ¹³C{¹H} NMR (MeOH-*d*₄, 100.62 MHz): δ 28.28 (s, COMe), 36.97 (s, CH₂CO), 39.92 (d, ³J(CP) 26.3 Hz, PdCOCH₂), 210.18 (s, COMe), 221.44 (d, ²J(CP) 7.5 Hz, COCH₂). ³¹P{¹H} NMR (MeOH-*d*₄, 161.98 MHz): δ 14.53 (s).

Reaction of 7a with C₂H₄ in 2,2,2-trifluoroethanol (TFE). A solution of **7a** (0.03 mmol) in a 3 : 1 (v/v) mixture of TFE/C₆D₆ was prepared following a procedure analogous to that reported above in MeOH-*d*₄. The solution was then transferred into a HP-NMR tube and pressurized with ethylene to 42.0 bar at room temperature (³¹P{¹H} NMR singlet at δ 21.50). The tube was gradually heated (10 °C steps) and ³¹P{¹H} NMR spectra were acquired at all temperatures. At 110 °C, **7a** started to convert most likely into a new alkyl species (³¹P{¹H} NMR singlet at δ 24.20). After 20 min, the HP-NMR tube was cooled to room temperature. The ³¹P{¹H} spectrum showed a *ca.* 50% conversion of **7a** into the new compound (δ 25.80). After removal of the tube from the

NMR probe, a thin layer of linear polyethylene located at the solid–gas interphase was visible in the tube. A GC–MS analysis of the solution showed no formation of oligomers.

Catalytic copolymerisation of CO and ethylene

Autoclave experiments in MeOH or TFE with 1a, 1b, 5a and 5b as catalyst precursors. Typically, MeOH (50 mL) or TFE (50 mL), was introduced by suction into an autoclave (200 mL), previously evacuated by a vacuum pump, containing the catalyst precursor (0.012 mmol palladium). When the catalytic reaction was performed in the presence of 1,4-benzoquinone (BQ) or *p*-toluenesulfonic acid monohydrate (TsOH), these compounds and the catalytic precursor were added together in the autoclave. The autoclave was then charged with the desired CO–C₂H₄ mixture to 42.0 bar at room temperature followed by heating to the desired temperature. Once the desired temperature was reached the total pressure of the gas mixture was equilibrated to 56.0 bar and stirring (1300 rpm) was started. After the desired reaction time, the autoclave was cooled by means of an ice–water bath and the gases released. Due to the much higher solubilizing capacity of TFE¹³ for the copolymer as compared to MeOH, two different procedures were employed to collect the copolymer products. For the experiments in MeOH, the insoluble copolymer was filtered off, washed with MeOH, and dried under vacuum at 60 °C to constant weight. For the experiments in TFE, the catalysis mixture was poured into MeOH (100 mL), followed by stirring for 30 min before filtering the solid product.

Operando HP-NMR studies performed in TFE/C₆D₆ with 5a and in MeOH-*d*₄ with 5b

A HP-NMR tube was charged with either a solution of **5a** (0.015 mmol) in TFE/C₆D₆ (3 : 1 (v : v), 2.0 mL) or a solution of **5b** (0.015 mmol) in MeOH-*d*₄ (2.0 mL) under nitrogen at room temperature. After ³¹P{¹H} and ¹H (only for the study with **5b** in MeOH-*d*₄) NMR spectra were recorded at room temperature, the tube was removed from the NMR probe head, charged with CO to 14.0 bar, and then placed again into the NMR probe at room temperature. After the NMR spectra were recorded, the tube was removed from the NMR probe and charged with ethylene to a total pressure of 56.0 bar. The tube was placed again into the NMR probe at room temperature and the catalytic reaction was followed by variable-temperature NMR spectroscopy in the temperature range from 20 to 110 °C. After 10 min at 110 °C, the tube was cooled to 20 °C, which was followed by the acquisition of NMR spectra. Once the sapphire tube was removed from the NMR probe, in the case of the NMR study employing **5a** an off-white layer of non-alternating copolymer over a yellow solution was observed, while in the case of **5b** a layer of grey non-alternating copolymer and a dark solution was observed.

X-Ray crystallographic data collection and refinement of the structure of 2b

X-Ray diffraction intensity data were collected on an Enraf Nonius CAD4 automatic diffractometer with graphite monochromator, employing Mo-*K*_α radiation at room temperature. Unit cell parameters of the structure were determined from a least-squares refinement of the setting angles of 25 carefully centred reflections.

An experimental absorption correction (psi-scan) was performed. All structure determination calculations were performed with the WINGX package^{20a} with SIR-97^{20b} SHELXL-97^{20c} and ORTEP-3 programs.^{20d} 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 respective carbon atoms. Crystallographic data of **2b** are reported in Table 1.

CCDC reference number for **2b**: 653758.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b711280g

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