

# Chapter 6

## New palladium complexes for alternating CO/*tert*-butylstyrene copolymerisation in supercritical carbon dioxide

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*The activity of new cationic palladium complexes with perfluorinated bipyridine and phenantroline ligands has been studied in the copolymerisation of 4-*tert*-butylstyrene with carbon monoxide in supercritical carbon dioxide. Highly syndiotactic polyketones were obtained. The molecular weight and polydispersity obtained for the polyketones in supercritical carbon dioxide are better than in conventional solvents.*

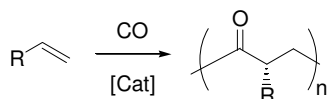
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*Manuscript in preparation: Marta Giménez-Pedrés, Anna M. Masdeu-Bultó, Maurizio Solinas and Walter Leitner, 2005*

## 6.1. Introduction

In the past few years interest has been a growing in synthesizing alternating polyketones of general formula [C(O)CH(R)CH<sub>2</sub>]<sub>n</sub> from carbon monoxide and olefins (Scheme 1) [1, 2, 3]. These polyketones are a class of low-cost thermoplastics whose synthesis, properties and applications are still the object of intense fundamental and applied research.

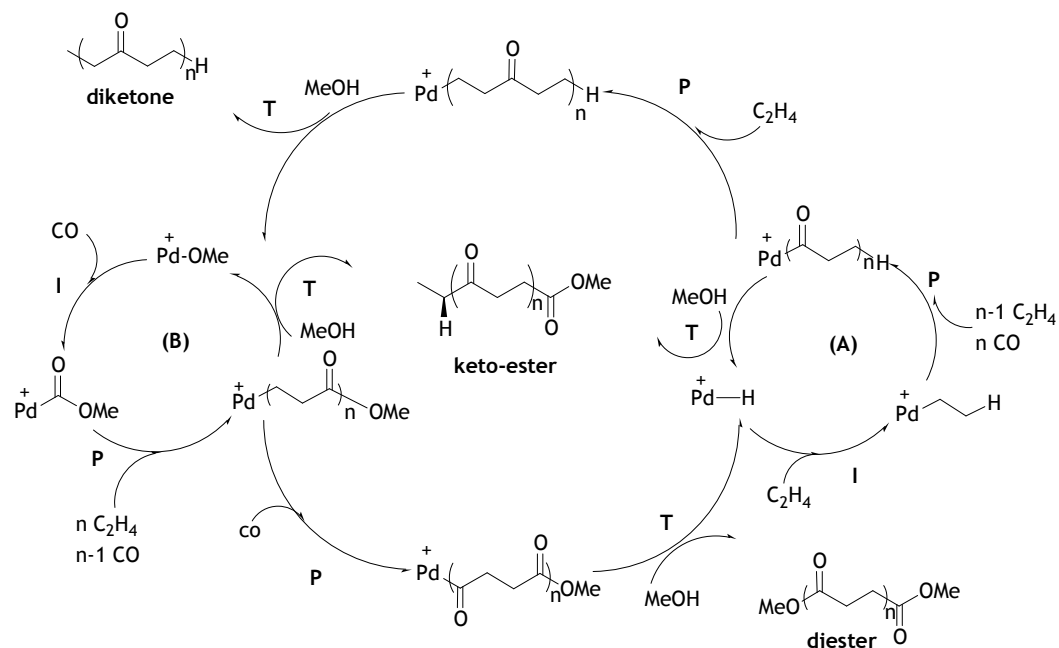


Scheme 1

The first example of metal-catalysed copolymerisation of ethene and carbon monoxide was based on nickel. In the late 1940s, Reppe and Magin showed that K<sub>2</sub>[Ni(CN)<sub>4</sub>] in water catalysed the production of low-melting polyketone oligomers in addition to diethylketone and propionic acid [4]. Palladium (II) dichloride complexes with monophosphines were first studied by Gough (ICI), and they showed moderate activity in harsh reaction conditions [5]. In the early 1980s Sen reported that cationic palladium (II) complexes containing monodentate phosphines and non-coordinating counteranions such as tetrafluoroborate produces polyketones in mild conditions but at low reaction rates [6, 7]. It was in 1982, that Drent (Shell) discovered that using bidentate phosphines as ligands and weak coordination counteranions in palladium (II) based catalyst obtained high molecular weight polyketones in relatively mild reaction conditions [8, 9].

In 1991, Drent et al. [9] made a careful study of the end groups and presented the first mechanistic interpretation of the copolymerisation of ethene and carbon monoxide in alcoholic solvents [3]. Since then several studies have been made in an attempt to understand this mechanism. In 1996, Drent and

Budzelaar [2] proposed the complete mechanism, which is applicable to other alkenes, for the copolymerisation of ethene and carbon monoxide (Scheme 2).

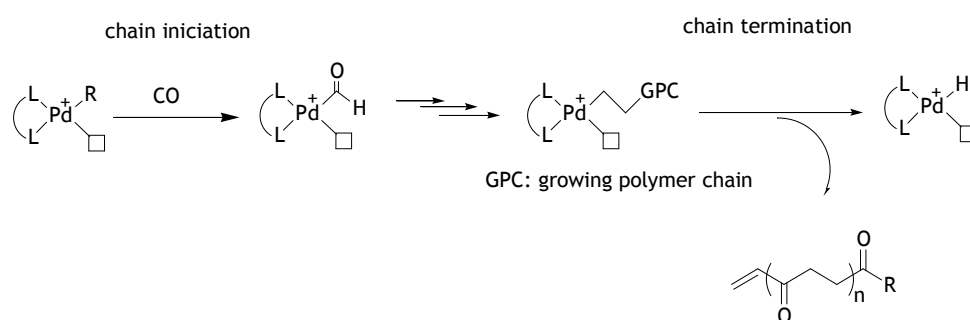


Scheme 2. Proposed mechanism for the copolymerisation of CO/ethene in methanol

Two competing cycles, connected by cross termination steps, would be simultaneously producing polyketones in methanol. The prevalence of either cycle is depending on the experimental conditions. Cycle A is initiated (I) with the insertion of ethene in the palladium hydride bond. The palladium hydride species can be generated in a variety of ways: by a  $\beta$ -hydrogen elimination from a palladium methoxide, a water-gas-shift reaction, a Wacker-type oxidation of ethene or a hydrogen activation (in the presence of hydrogen). Propagation (P) occurs by migratory reversible insertion of CO into the ethyl complex followed by the irreversible migratory insertion of ethene into the palladium acyl bond leading to perfect alternating polyketones. No

propagation errors (double CO or olefin sequences) are observed in this kind of copolymers. Double CO insertion will not occur for thermodynamic reasons, while double ethene insertion is kinetically hampered because palladium (II) centers have a greater affinity for CO than for ethene [10, 11]. The copolymer formed by this cycle has either keto-ester or diketone end groups. The terminal structure depends on the termination path (T). The keto-ester structure is obtained by methanolysis of a Pd-acyl bond, and the diketone structure is obtained if a protonolysis occurs in a Pd-acyl bond.

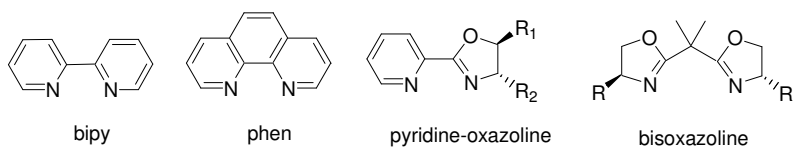
Cycle (B) starts with the palladium carbomethoxy species, which are formed either by a CO insertion into a palladium methoxide or by a methanol direct attacking on coordinated CO. The propagation steps enable the chain to grown. This cycle also shows two different end groups: keto-ester, formed via protonolysis in a Pd-alkyl bond, or diester via methanolysis of a Pd-acyl bond. When the copolymerisation reaction is preformed in non-protic solvents, an alkylpalladium species is necessary so that the first monomer can be inserted (Scheme 3). Termination occurs in this case by  $\beta$ -elimination, which forms Pd-H species and unsaturated-end groups. This pathway is also the main termination step in such alkenes as propene and styrene.



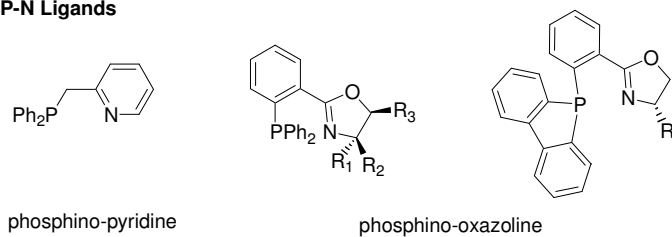
Scheme 3. Initiation and termination steps using an alkylpalladium catalyst in a non-protic solvent

Unlike CO/ethene or CO/propene copolymerisation, catalysts containing diphosphine ligands are not active in the copolymerisation of styrene and their derivatives with carbon monoxide, since low molecular weight oligomers are obtained [2, 12]. This is because  $\beta$ -H elimination is favoured rather than polymer chain growth because the electron density around the metal is higher when a phosphine is coordinated to palladium than to nitrogen ligands [2, 3]. Moreover, the palladium styryl intermediates are strongly stabilized by  $\pi$ -benzylic coordination and so CO insertion is inhibited [13]. However, the unsymmetrical bidentate phosphine-phosphite ligand, (R,S)-BINAPHOS (Figure 1) has been applied to *tert*-butylstyrene/CO copolymerisation [14]. But in general, the most effective system for copolymerising styrene and its derivatives with CO is to use preformed cationic palladium catalyst associated with N-N chelating ligands (Figure 1) such as bipyridine, phenantroline, pyridine-oxazoline or bisoxazoline and weakly coordinating anions [15-18]. Chelating P-N ligands have been also applied to catalysed copolymerisation, although severe reaction conditions are needed to obtain polyketones [19,20]. In the copolymerisation of styrene with carbon monoxide, two additional aspects must be considered: the regioselectivity and the stereoselectivity. Styrene can be inserted into palladium-acyl intermediates either in primary (1,2-insertion) or secondary mode (2,1-insertion) (Scheme 4). Three different arrangements in the polymer structure are possible: tail-to-tail, head-to-tail or head-to head. The styrene is inserted only in secondary mode when bisnitrogen donor ligands are used and head-to tail polymers are obtained. However, the insertion is in primary mode when (R, S)-BINAPHOS is used as a ligand. This mode of insertion also prevents  $\beta$ -H elimination and might explain the activity of this ligand in CO/styrene copolymerisation [21]. A mixture of both insertion modes is observed when P-N ligands are used [20].

**N-N Ligands**



**P-N Ligands**



**P-P Ligands**

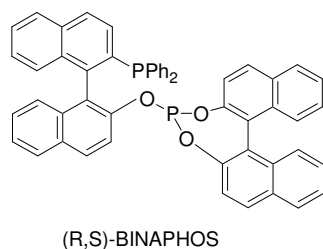
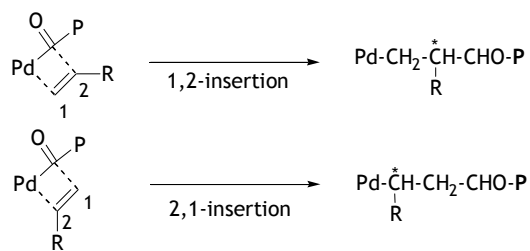


Figure 1. Ligands reported in CO/styrene copolymerisation



Scheme 4

The stereochemistry of the alkene insertion along the chain determines the copolymer tacticity: atactic (stereoirregular), syndiotactic (RSRSRS sequence) or isotactic (RRRRR or SSSSSS sequence) copolymers can be obtained (Figure 2).

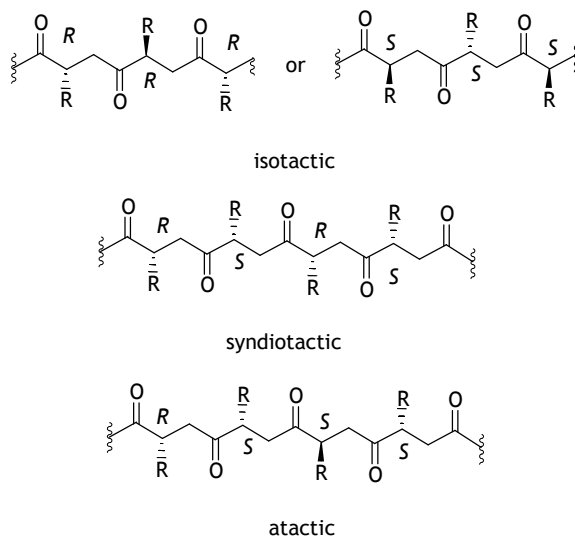
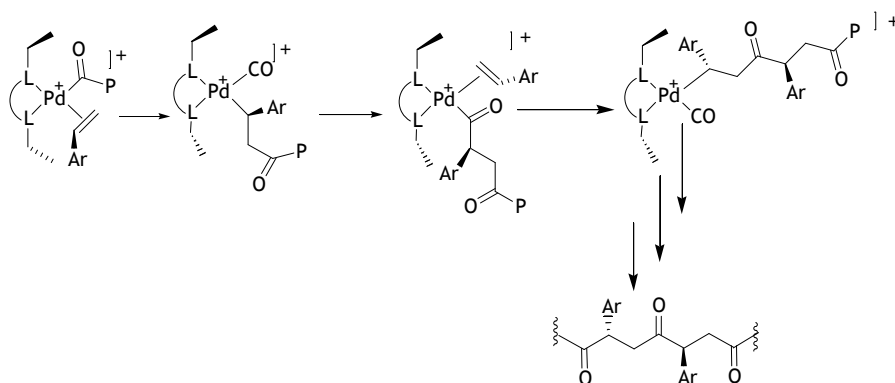


Figure 2. Tacticity of CO/alkene copolymers

Two different mechanisms provide stereoregular copolymers (syndiotactic or isotactic). When a chiral ligand is used, the enantiomeric environment created by the ligand will control the stereoregularity of the styrene insertion. This mechanism is known as *site control* and provides isotactic polymers. When non-chiral ligands are used, the growing polymer chain, which is chiral, controls the stereoregularity of styrene insertion and leads this case to syndiotactic polymers. This mechanism is known as *chain-end control* (Figure 3).

## Site Control



## Chain Control

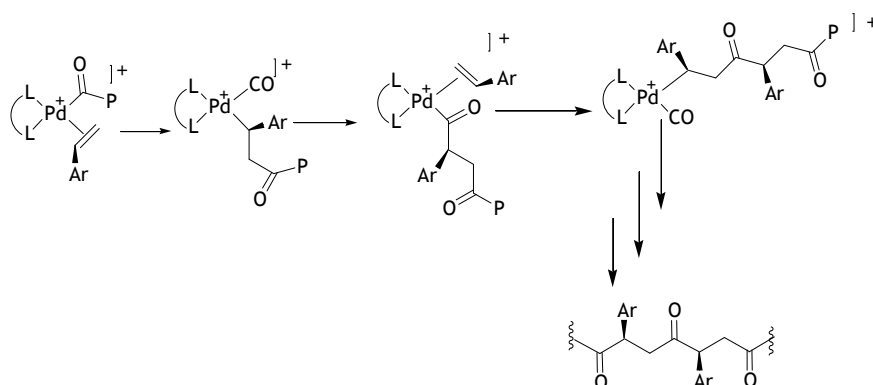


Figure 3

Normally, copolymerisation reactions are carried out with conventional organic solvents, such as methanol, trifluoroethanol or chlorobenzene. During the last years, supercritical carbon dioxide has emerged as an alternative solvent for polymerization reactions [22]. As well as the environmental advantages already discussed, the separation of the solvent from the reaction product is simpler since CO<sub>2</sub> reverts to the gaseous state upon depressurisation, and this results in a dry polymer product. This feature eliminates the energy intensive drying steps required to remove the solvent in polymer manufacturing and may save both money and energy. ScCO<sub>2</sub> can also



be used in polymer processing techniques such as plasticisation, impregnation or polymer extraction and purification [23].

Solubility plays an important role in polymerisation reactions in scCO<sub>2</sub>. While carbon dioxide is a good solvent for non-polar low molecular weight molecules, it is a poor solvent for high molecular weight polymers. In fact, the only polymers that are highly soluble in scCO<sub>2</sub> are fluoropolymers and silicones [24]. This makes it possible to synthesize of high molecular weight fluoropolymers by homogeneous solution polymerisation in scCO<sub>2</sub> [25].

The use of transition metal catalysis for precipitation polymerisations has been studied in supercritical carbon dioxide. DeSimone et al. studied [26] the ring-opening metathesis polymerisation (ROMP) of norbornene in scCO<sub>2</sub> with a [Ru(H<sub>2</sub>O)<sub>6</sub>](*p*-O<sub>3</sub>SC<sub>6</sub>H<sub>4</sub>Me)<sub>2</sub> catalyst which, although insoluble in scCO<sub>2</sub>, was solubilized by adding methanol as a co-solvent. The molecular weights and polydispersities were similar to those obtained without methanol but the yields increased when methanol was used as co-solvent. The presence of methanol had a considerable effect on the microstructure of the polymer. Fürstner et al. [27] reported even higher activities in the polymerisation of norbornene, when they used ruthenium and molybdenum catalysts (Figure 4). The ruthenium catalyst was also used to polymerise cis-cyclooctadiene. Both catalysts produced high molecular weight polymers (10<sup>5</sup>-10<sup>6</sup> g·mol<sup>-1</sup>) in good yields up to 94 %.

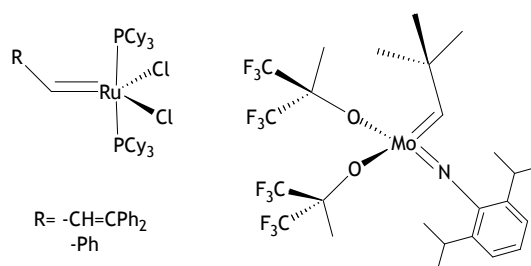


Figure 4.

De Vries et al. [28] studied the polymerisation of 1-hexene and ethene in  $\text{scCO}_2$  with cationic palladium catalyst (Figure 5a). The catalyst was soluble in  $\text{scCO}_2$  probably because BARF was used as counteranion and the polymer precipitated in the reaction media. The results showed that the activities and molecular weight distributions were similar to those obtained when dichloromethane was used as a solvent.

The synthesis of polyketones has hardly been studied in supercritical carbon dioxide. The first example was reported by Kläui and co-workers [29] for the copolymerisation of CO/ethene with a nickel catalyst (Figure 5b). The results showed the formation of a strictly alternating copolymer in  $\text{scCO}_2$ .

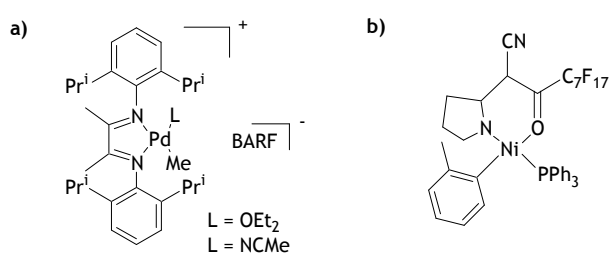


Figure 5.

Nozaki et al. [30] reported the copolymerisation of  $\omega$ -perfluoroalkyl alkenes with CO in  $\text{scCO}_2$  catalyzed by Pd(II)-(R,S)-BINAPHOS. When the ligand was not modified, no conversion was observed. Inserting a perfluorinated chain into the ligand makes the catalyst soluble in  $\text{scCO}_2$ , but the reported yield is only 3%.

The present chapter describes the first example known to date of the copolymerisation of *tert*-butylstyrene with CO in supercritical carbon dioxide as a reaction media catalysed by cationic palladium complexes, which contain the bipyridine and phenantroline ligands with perfluorinated chains, 1 and 2 (Figure 6).

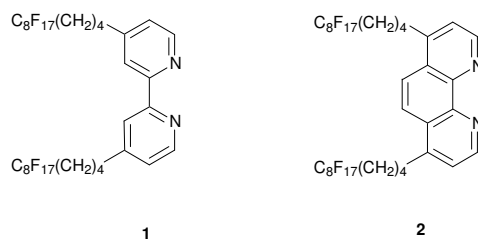
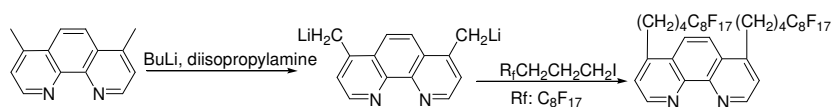


Figure 6. Ligands 1 and 2

## 6.2. Results and discussion

### Synthesis of ligands

In an attempt to obtain a catalyst that was both active and soluble in supercritical carbon dioxide we decided to synthesize ligands containing perfluorinated chains. The synthesis of perfluorinated ligand **1** was described by Pozzi et al. [31]. Ligand **2** was prepared with a similar procedure by reaction of 4,7'-dimethylphenanthroline with butyllithium and diisopropylamine and then reaction with 3-perfluorooctyl-1-iodopropane (Scheme 5). Ligand **2** was obtained as a brown solid in a moderate yield (32%).

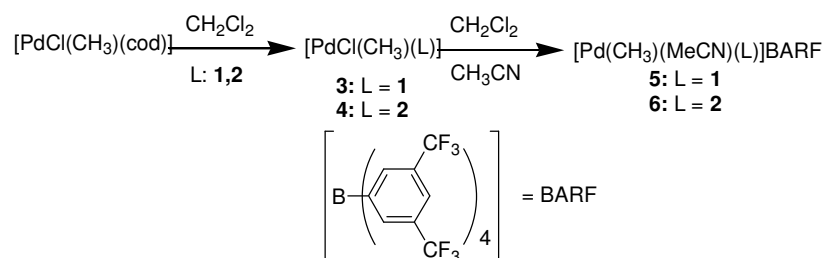
Scheme 5. Synthesis of **2**

The  $^1H$  NMR spectrum of **2** shows the three different methylenic signals at  $\delta$  1.78 ppm ( $-CH_2-CH_2-$ ),  $\delta$  2.08 ppm ( $-CH_2-R_f$ ) and  $\delta$  3.14 ppm (Phen- $CH_2$ ). The signals corresponding to the aromatic protons of the phenanthroline appear at  $\delta$  7.38, 7.98 and 9.02 ppm. The  $^{19}F$  NMR spectra show the signal of the  $CF_3$  at  $\delta$  -81.17 and the signals of  $CF_2$  appear between  $\delta$  -114.14 and -126.57 ppm.

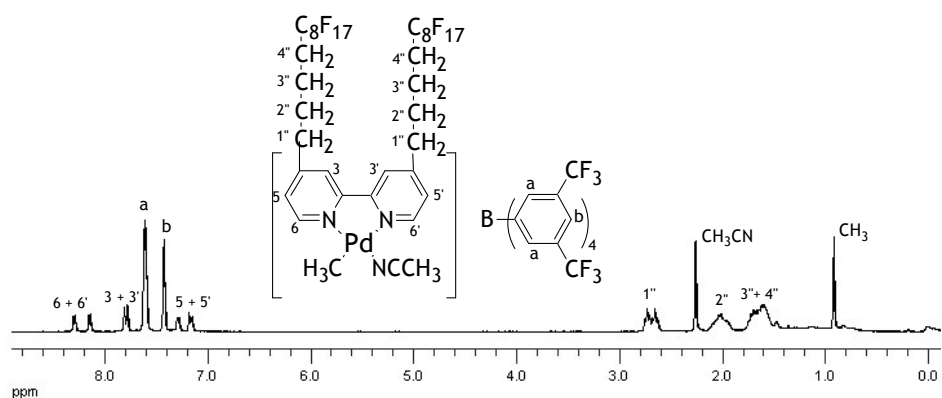
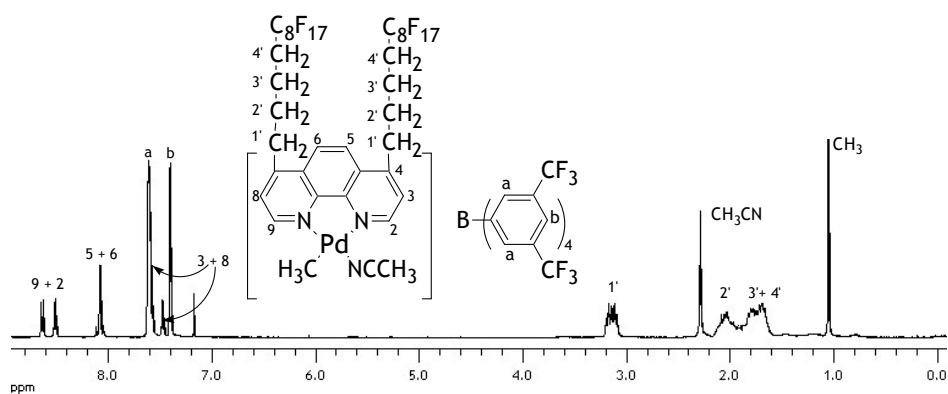
*Synthesis of palladium complexes*

The neutral palladium complexes  $[\text{PdCl}(\text{CH}_3)(\text{L})]$  (3: L = 1 and 4: L = 2) were prepared by stoichiometric reaction of  $[\text{PdCl}(\text{CH}_3)(\text{cod})]$  (cod = 1,5-cyclooctadiene) with the corresponding ligand in anhydrous dichloromethane (Scheme 6). The neutral palladium complexes were not soluble in common deuterated solvents, so the structure was confirmed by mass spectrometry (EI). Complex 3 shows the signal at  $m/z = 1210.0$ , corresponding to  $[\text{M}-\text{Cl}-\text{CH}_3]^+$ , and complex 4 shows the signal at  $m/z = 1234.9$  corresponding to  $[\text{M}+\text{H}-\text{Cl}-\text{CH}_3]^+$ .

Cationic palladium complexes  $[\text{Pd}(\text{CH}_3)(\text{NCCH}_3)(\text{L})]\text{BARF}$  (5: L = 1 and 6: L = 2, BARF =  $\text{B}(\text{3,5}-(\text{CF}_3)_2\text{C}_6\text{H}_3)_4^-$ ) were prepared by reaction of NaBARF in the presence of  $\text{CH}_3\text{CN}$  and  $\text{CH}_2\text{Cl}_2$  (Scheme 6). The  $^1\text{H}$  NMR spectra of complexes 5 and 6 (Figure 7 and 8 respectively) show the signal corresponding to the coordinated methyl around  $\delta$  1 ppm and the signal of coordinated acetonitrile ca.  $\delta$  2.32 ppm. The aromatic region shows the signals corresponding to the counteranion at  $\delta$  7.0 and 7.7, and the six signals corresponding to non-equivalent protons of the bipyridine or phenantroline ring between 7.4-8.4 ppm. The  $^{19}\text{F}$  NMR spectra show the signals corresponding to the perfluorinated chain and the signal corresponding to the counteranion around  $\delta$  -63 ppm.



Scheme 6 Synthesis of complexes 3-6.

Figure 7.  $^1H$  NMR spectra of **5**Figure 8.  $^1H$  NMR spectra and **6**

#### Solubility of catalyst precursors in $scCO_2$

The solubility of catalyst precursors **5** and **6** was studied using a 10 ml window-equipped-stainless steel autoclave. The autoclave was charged under argon with 0.0125 mmol of the preformed catalyst **5** or **6**, and then *tert*-butylstyrene (7.75 mmol) was added. The autoclave was filled with CO (1-5 bar), pressurised with carbon dioxide (150- 250 bar) and heated at 37°C.

Visual inspection through the windows showed a homogeneous orange solution even in liquid carbon dioxide. (Figure 9a)

*Copolymerisation of 4-tert-butylstyrene with CO in  $scCO_2$*

The catalysis was performed using the preformed cationic complexes 5 and 6 in a 10 ml window equipped stainless steel autoclave. The solubility of the palladium complexes in supercritical carbon dioxide was monitored by visual inspection. Both catalyst precursors were soluble in both liquid and supercritical carbon dioxide. As expected, the polyketone was not soluble in  $scCO_2$  and precipitates during the reaction (Figure 9b).

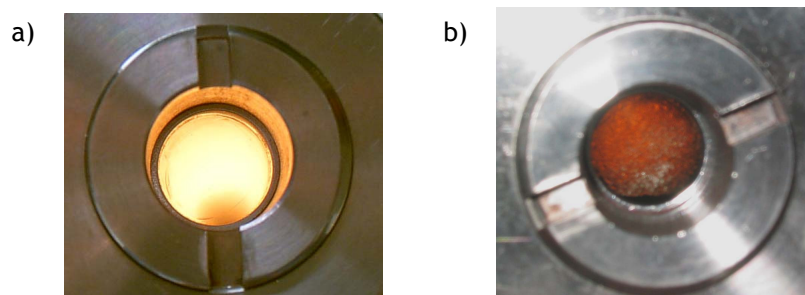


Figure 9.a) Complex 6 solubilized in reaction conditions (5 bar, 250 bar  $CO_2$ )  
b) during the polymerisation using complex 5. The white solid on the windows is the precipitated polymer.

We also tested the solubility and the activity of the unmodified  $[Pd(CH_3)(NCCH_3)(L)]BARF$ , (L: 4-4'-dimethylpyridine). The catalyst was not soluble in the conditions studied (3.4 bar of CO and 145 bar of  $CO_2$ ), and no polyketone was produced. This clearly showed that a soluble catalyst is required if the activity for copolymerisation in  $scCO_2$  is to be acceptable.

The results of copolymerising 4-*tert*-butylstyrene with CO/ using complexes **5** and **6** are listed in Table 1. Some experiments using dichloromethane as solvent were carried out to compare the activity in homogeneous catalysis. Partial pressures of carbon monoxide between 1-5 bar were tested. The effect of carbon dioxide pressure on the activity and the molecular weight was also studied. The polymers obtained were characterised by <sup>1</sup>H and <sup>31</sup>C NMR. Figure 10 shows the <sup>13</sup>C NMR spectra of the methylene carbon atom corresponding to different experiments are shown. As a reference an epimerized sample of copolymer is shown. These spectra are consistent with a high syndiotactic copolymer structure (81-90 uu% diads).

Using 1 bar pressure of carbon monoxide (entry 1 and 2, Table 1), productivities were low for both dichloromethane and supercritical carbon dioxide as solvents, although molecular weights were higher in scCO<sub>2</sub>. When the partial pressure of carbon monoxide was increased, both activity and molecular weight were enhanced (entries 2, 3 and 5, Table 1).

Table 1 Copolymerization of CO/TBS in supercritical carbon dioxide using **5** or **6** as catalyst precursor<sup>a</sup>

Entry	Precursor	Time(h)	Productivity [g CP/(g Pd x h)]	P(CO) bar	P(CO <sub>2</sub> ) bar	Mw (Mw/Mn) <sup>d</sup>
1 <sup>b</sup>	<b>5</b>	24	1.79	1	-	6328(1.3)
2	<b>5</b>	24	2.18	1	150	8863 (1.0)
3	<b>5</b>	24	5.79	3.5	170	11130 (1.8)
4 <sup>b</sup>	<b>5</b>	24	12.14	5	-	43740 (5.3)
5	<b>5</b>	24	11.21	5	170	56130 (1.5)
6	<b>5</b>	16	15.25	5	200	63000 (1.8)
7	<b>5</b>	24	9.75	5	250	87820 (1.2)
8 <sup>c</sup>	<b>5</b>	24	10.69	5	250	39740 (1.3)
9	<b>6</b>	24	8.55	5	250	28078 (1.5)

<sup>a</sup> Reaction Conditions: 0.0125 mmol catalyst, substrate/cat = 620, T=37°C <sup>b</sup> CH<sub>2</sub>Cl<sub>2</sub> was used as a solvent, T= 25 °C; <sup>c</sup> no stirring <sup>d</sup> Mw: Molecular weight, Mw/Mn: polydispersity

At 5 bar of CO, when the total pressure of scCO<sub>2</sub> was increased from 170 to 250 bar the molecular weight ( $M_w$ ) increased up to twice the value obtained in dichloromethane with the same catalyst precursor (entry 7 vs 4, Table 1). Moreover, the distribution of molecular weight was very narrow in scCO<sub>2</sub>. The polydispersity decreased from 5.3 in dichloromethane to 1.2 in scCO<sub>2</sub>. This positive effect was attributed to the high miscibility of CO in scCO<sub>2</sub>. The CO is efficiently dissolved and then the gas-liquid mass transfer disappears so the growing chain step could be favoured and  $\beta$ -elimination avoided. Also, the polydispersity is decreased because the polymer precipitates from solution. Taking advantage of the high diffusivity of supercritical carbon dioxide, we decided to perform one test without stirring. The productivity was similar but the molecular weight decreased by half (entry 8, Table 1).



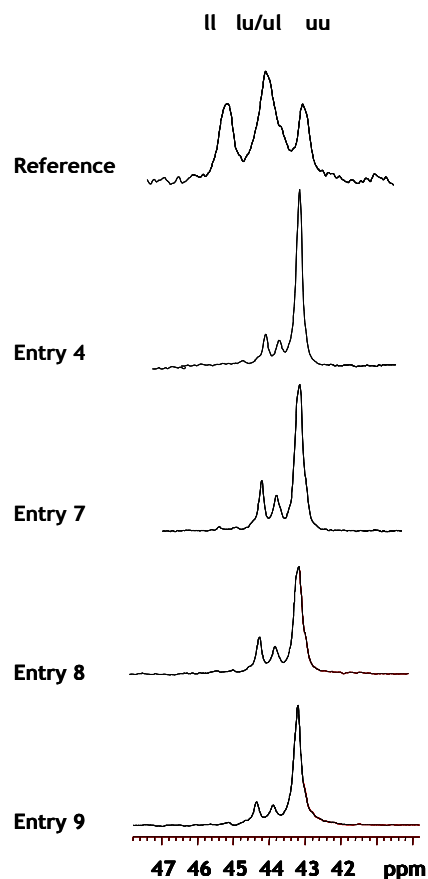


Figure 10. <sup>13</sup>C NMR spectrum in the region of methylene carbon atom corresponding to the copolymer obtained (Table 1)

We also explored the possibility of using supercritical carbon dioxide to extract the catalyst and the unreacted substrate from the polyketone. The extraction was performed by flushing supercritical carbon dioxide between (180-200 bar) through the autoclave for 1h and 15 minutes. The catalyst and the unreacted substrate were collected in two cold traps at -78°C (Figure 11). At the end of the extraction the cold traps contain a mixture not quantified of catalyst and *tert*-butylstyrene.

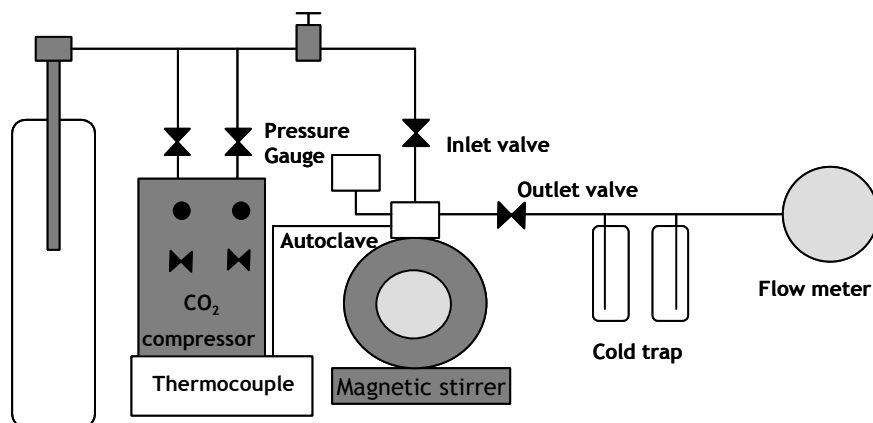


Figure 11. Schematic representation of the extraction of catalyst and unreacted substrate

### 6.3. Conclusions

In conclusion, we showed that CO/TBS could be copolymerised using supercritical carbon dioxide and that there is no need to use toxic organic solvents. Moreover, the polyketones obtained are highly syndiotactic and have higher molecular weights and improved polydispersities. Preliminary experiments suggest that the catalyst can be separated by extraction with supercritical CO<sub>2</sub>.

### 6.4. Experimental part

All reactions were carried out in a nitrogen atmosphere at room temperature using standard Schlenk techniques. Solvents were distilled and deoxygenated prior to use. The salt NaBAR<sup>4</sup> (Ar<sup>3</sup>=3, 5-(CF<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>) was prepared according to reported methods [32]. Ligand 1 was prepared according to a published method [31].

NMR spectra were recorded on a Varian Gemini spectrometer operating at <sup>1</sup>H (300 or 400 MHz), <sup>13</sup>C (75.43 or 100.57 MHz), <sup>19</sup>F (376.3 Hz). Chemical shifts were reported relative to tetramethylsilane for <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} as internal

reference. Mass spectrometry was performed in an AUTOSPEC spectrometer (EI-HR) and AUTOFLEX spectrometer (MALDI-TOF).

The molecular weight of the copolymers and molecular weight distributions were determined by gel permeation chromatography (GPC -MALLS). The measurements were made in THF on an Agilent 1100 series using a four-serial column system MZ Gel DVB gel-permeation chromatography device with a Wyatt DAWN Light Scattering and an Optilab (Wyatt Technology) refractive index detector or by gel permeation chromatography (GPC) in  $\text{CHCl}_3$  on a Waters 515-GPC device using a linear Waters Ultrastyrigel column with a Waters 2410 refractive index detector and polystyrene standards.

#### *Synthesis of 4,7'-bis[4''-(F-octyl)-butyl]-1,10'-phenantroline (2)*

A solution of n-butyllithium 1.6 M in hexane (10.5 ml, 16.8 mmol) was added, via a syringe, to a solution of diisopropylamine (2.7 ml, 19.2 mmol) in tetrahydrofuran (5 ml) at  $-78^\circ\text{C}$ . The solution was stirred for 20 min. at  $-78^\circ\text{C}$  and 4,7'-dimethylphenantroline (1g, 4.8 mmol) in 75 ml of tetrahydrofuran was then added dropwise. The dark brown solution was stirred at  $-78^\circ\text{C}$  for 1h. Then, 3-perfluorooctyl-1-iodopropane (6.77 g, 11.52 mmol) in 50 ml of tetrahydrofuran was added slowly via a syringe at  $-78^\circ\text{C}$ . The violet solution was stirred for 5h at  $-78^\circ\text{C}$  and at room temperature overnight. The solvent was removed under reduced pressure. Then, 60 ml of water were added and the mixture was extracted (2 x 75 ml) of diethylether, and with dichloromethane (2 x 75 ml). The organic extracts were collected and dried over  $\text{Mg}_2\text{SO}_4$ . The solvent was removed under reduced pressure and the residue was recrystallized from dichloromethane/pentane. The product was obtained as a brown solid. 1.76 g, (Yield = 32 %).

$^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ ):  $\delta$  1.78 (dm, 8H;  $(\text{H}_2\text{C})_{3'-4'}$ ), 2.08 (m, 4H,  $(\text{H}_2\text{C})_{2'}$ ), 3.14 (t, 4H,  $(\text{H}_2\text{C})_{1''}$ ,  $^2J = 7.6$ ); 7.38 (d, 2H,  $\text{H}_{3,8}$ ,  $^3J = 4.5$  Hz), 7.98 (s, 2H,  $\text{H}_{5,6}$ ), 9.02 (d,  $^3J = 4.8$  Hz, 2H,  $\text{H}_{2,9}$ );  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ) :  $\delta$ -81.17 ( $\text{CF}_3$ ), -114.15 ( $\text{CF}_2$ ), -122.39 ( $\text{CF}_2$ ), -123.17 ( $\text{CF}_2$ ), -123.85 ( $\text{CF}_2$ ), -126.57 ( $\text{CF}_2$ ).

EIMS  $m/z$ : 1129.3  $[\text{M} + \text{H}]^+$ . High resolution EIMS:1129.13,  $\text{C}_{36}\text{H}_{23}\text{F}_{34}\text{N}_2$

*Synthesis of [PdClMe(1)] (3).*

A solution of 4,4'-bis[4''-(F-octyl)-butyl]-2,2'-bipyridine (250 mg, 0.2265 mmol) in 10 ml of dichloromethane was added to a solution of [PdClMe(cod)] (50 mg, 0.1887 mmol) in 1 ml of dichloromethane. The yellow mixture was stirred at room temperature for 3.5 h. The complex was filtered off and washed with dichloromethane. This complex was not soluble enough in common deuterated solvents to allow its NMR spectra to be recorded. 0.27 g, (Yield =96 %)

EIMS  $m/z$ : 1210.0  $[\text{M}-\text{Cl}-\text{CH}_3]^+$ , 1105.2  $[1+1]$

*Synthesis of [PdClMe(2)](4).*

A solution of 4,7'- bis[4''-(F-octyl)-butyl]-1,10-phenantroline (300 mg, 0.2659 mmol) in 10 ml of dichloromethane, was added to a solution of [PdClMe(cod)] (70 mg, 0.2642 mmol) in 5 ml of dichloromethane. The mixture was stirred at room temperature for 3.5h. The product was filtered off and washed with dichloromethane. This complex was not soluble enough in common deuterated solvents to allow its NMR spectra to be recorded. 0.30 g, (Yield = 87 %)

EIMS  $m/z$ : 1234.9  $[\text{M} + \text{H}-\text{Cl}-\text{CH}_3]^+$ .

*Synthesis of [PdMe(NCMe)(1)][BARF] (5).*

To a suspension of [4,4'-di-[4''-(F-octyl)-butyl]-2,2'-bipyridyl]chloromethyl-palladium (II) (61 mg, 0.048 mmol) in 5 ml of dichloromethane, sodium tetrakis 3,5-bis-(trifluoromethyl)phenyl borate (40.5 mg, 0.048mmol) and 0.3 ml of acetonitril were added. The mixture was heated for 1h at 40 C. The product was filtered off over celite and the solvent was removed under reduced pressure. The product was obtained as an oil. 77.7 mg (Yield = 78 %)

$^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  0.97 (s, 3H,  $\text{CH}_3$ ) 1.71 (2m, 8H,  $(\text{CH}_2)_{3''-4''}$ ), 2.10 (m, 4H,  $(\text{CH}_2)_{2''}$ ), 2.32 (s, 3H,  $\text{CH}_3\text{CN}$ ), 2.74 (dt, 4H,  $(\text{CH}_2)_{1''}$ ,  $^2J = 7.6$  Hz), 7.23 (d, 1H,  $J = 5.2$  Hz), 7.34 (d, 1H,  $J = 5.2$  Hz), 7.50 (s, 4H,  $\text{BAr}'$ ), 7.68 (s, 8H,  $\text{BAr}'$ ), 7.85 (s, 1H), 7.87 (s, 1H), 8.23 (d,  $J = 5.2$  Hz, 1H), 8.36 (d,  $J = 5.6$  Hz, 1H);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ) :  $\delta$  -62.95 ( $\text{CF}_3$ ,  $\text{BARF}$ ), -81.43 ( $\text{CF}_3$ ), -114.93 ( $\text{CF}_2$ ), -122.51 ( $\text{CF}_2$ ), -123.31 ( $\text{CF}_2$ ), -124.15 ( $\text{CF}_2$ ), -126.73 ( $\text{CF}_2$ ).

#### *Synthesis of $[\text{PdMe}(\text{NCMe})(2)][\text{BARF}]$ (6)*

To a suspension of 4,7'-bis[4''-(F-octyl)-butyl]-1,10'-phenantroline (62.2 mg, 0.048 mmol) in 5 ml of dichloromethane, sodium tetrakis 3,5-bis(trifluoromethyl)phenyl borate (40.5 mg, 0.048mmol) and 0.3 ml of acetonitril were added. The mixture was heated for 1h at 40 C. The product was filtered off over celite and the solvent was removed under reduced pressure. The product was obtained as an oil. 97.1 mg (Yield= 95 %)

$\delta$   $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ ): 1.05 (s, 3H,  $\text{CH}_3$ ), 1.74 (2m, 8H;  $(\text{CH}_2)_{3''-4''}$ ), 2.05 (m, 4H,  $(\text{CH}_2)_{2''}$ ), 2.29 (s, 3H,  $\text{CH}_3\text{CN}$ ), 3.12 (t, 2H,  $(\text{CH}_2)_{1''}$ ,  $^2J = 7.8$  Hz), 3.17 (t, 2H,  $(\text{CH}_2)_{1''}$ ,  $^2J = 7.2$  Hz), 7.04 (s, 4H,  $\text{BAr}'$ ), 7.48 (d, 1H,  $J = 5,1$  Hz), 7.57 (d overlapped, 1H), 7.61 (s, 8H,  $\text{BAr}'$ ), 8.08 (d, 2H,  $J = 2,4$  Hz), 8.51 (d, 1H,  $J = 5,1$  Hz), 8.64 (d,  $J = 5.7$  Hz, 1H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -62.95 ( $\text{CF}_3$ ,  $\text{BARF}$ ), -81.28 ( $\text{CF}_3$ ), -114.74 ( $\text{CF}_2$ ), -122.43 ( $\text{CF}_2$ ), -123.22 ( $\text{CF}_2$ ), -124.04 ( $\text{CF}_2$ ), -126.65 ( $\text{CF}_2$ ).

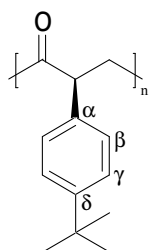
#### *CO/TBS copolymerisation experiments*

In standard catalytic experiment, a stainless steel high pressure reactor ( $V = 10$  ml) equipped with thick-wall glass windows was filled under argon with a solution of catalyst precursor **5** or **6** (0.0125 mmol) in 2 ml of  $\text{CH}_2\text{Cl}_2$ . The solvent was removed in vacuum and then *tert*-butylstyrene (1.24 g, 7.75 mmol) was introduced into the reactor under argon. The reactor was charged with CO and  $\text{CO}_2$  up to the desired pressure. The reactor was heated to 37 °C and stirred throughout the reaction. After the reaction, the autoclave was

cooled to room temperature and was carefully vented. The copolymer obtained was dissolved in  $\text{CH}_2\text{Cl}_2$  and precipitated by pouring the solution into 800 ml of rapidly stirred methanol. The product was filtered off, washed with methanol and vacuum dried.

#### Copolymer characterization

$\delta$   $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  7.02 (d,  $^3J = 8.0\text{Hz}$ , 2H,  $\text{H}_\beta$  or  $\text{H}_\gamma$ ), 6.62 (d,  $^3J = 8.0\text{ Hz}$ , 2H,  $\text{H}_\gamma$  or  $\text{H}_\beta$ ), 4.14 (t,  $^3J = 6.0\text{ Hz}$ , 1H, CH), 3.03 (dd,  $^2J = 17.6\text{ Hz}$ ,  $^3J = 6.4\text{ Hz}$ , 1H,  $\text{CH}_2$ ), 2.64 (dd,  $^2J = 17.6\text{ Hz}$ ,  $^3J = 6.4\text{ Hz}$ , 1H,  $\text{CH}_2$ ), 1.25 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  206.86 ( $-\text{C}(\text{O})-$ ), 149.76 ( $\text{C}_\delta$ ), 134.26 ( $\text{C}_\alpha$ ), 128.20 ( $\text{C}_\gamma$ ), 125.61 ( $\text{C}_\beta$ ), 52.86 (CH), 43.21 ( $\text{CH}_2$ ), 34.48 ( $\text{C}(\text{CH}_3)_3$ ), 31.48 ( $\text{C}(\text{CH}_3)_3$ ).



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