The *o*-methoxy groups on the P-aryl rings effect in the carbon monoxide and ethene copolymerisation reaction by palladium(II)-diphosphine catalysts. A mechanistic study

Abstract

In this chapter, relevant steps in the CO/ethene copolymerisation reaction, such as the migratory insertion of [Pd(Me)(CO)(P-P)]BArF (ArF = 3,5-$(CF_3)_2$-C_6H_3) and the carbonylation of the β-keto chelates [Pd(CH_2CH_2C(O)Me)(P-P)]BArF have been studied by *in situ* HP-NMR spectroscopy. The (P-P) ligands used in this study were the 1,2-bis(di(2-methoxyphenyl)phosphino)ethane (MeO-dppe) and the 1,3-bis(di(2-methoxyphenyl)phosphino)propane) (MeO-dppp).

This study contributes to rationalise the higher catalytic activity of palladium(II) catalysts modified with *o*-methoxy substituted diphosphine ligands as compared to analogous palladium(II) catalysts with 1,2-bis(diphenylphosphino)ethane (dppe) and 1,3-bis(diphenylphosphino)propane (dppp) ligands.

NMR studies have shown that the presence of *o*-MeO substituents on the P-aryl rings affects the kinetics of the CO/ethene copolymerisation. Unlike the catalysts with the dppe and dppp ligands, the rate of carbonylation of the *o*-MeO-modified β-keto chelates is limited by the Pd(alkyl)(CO) migratory insertion, which makes the overall copolymerisation process independent of the CO pressure.

Chapter 2

2.2.1. Introduction

As described in *chapter 1*, perfectly alternating polyketones are high-performance thermoplastics obtainable by copolymerisation of carbon monoxide and alkenes, generally ethene, in the presence of Pd(II) catalysts modified with chelating diphosphines (**Scheme 1,** *chapter 2*, section 2.1, pag. 66).[1] The copolymerisation reactions are commonly performed in protic solvents (alcohols, preferentially methanol), yet aprotic solvents such as CH_2Cl_2 are used in reactions catalysed by palladium(II) alkyl precursors as well as in model mechanistic studies.[2]

In section 2.1 (pag. 67) we presented that the introduction of one *o*-methoxy substituent on each P-aryl ring of the ligand greatly enhances the productivity as compared to reactions promoted by catalysts with unsubstituted diphosphines.[3,2d] Both steric and electronic factors have been invoked to account for the positive effect of the *o*-methoxy groups on the catalyst activity, yet no clear-cut explanation has been put forward so far. Indeed, most of the previous hypotheses are based on indirect observations such as the decreased formation of catalytically inactive bis-chelates or binuclear species;[4] the reduced tendency to phosphine oxidation;[5a] the increased basicity of the metal center;[5b] and the reduced stability of catalyst resting states.[5c]

Intrigued by the possibility of elucidating the *o*-methoxy effect, it was decided to look at two well-known reactions occurring during the propagation step of the alternating CO/C_2H_4 copolymerisation: i) the migratory insertion of $[Pd(Me)(CO)(P-P)]^+$ complexes and ii) the carbonylation of the β-keto chelates $[Pd(CH_2CH_2C(O)Me)(P-P)]^+$ (**Scheme 1**).[5b,5c]
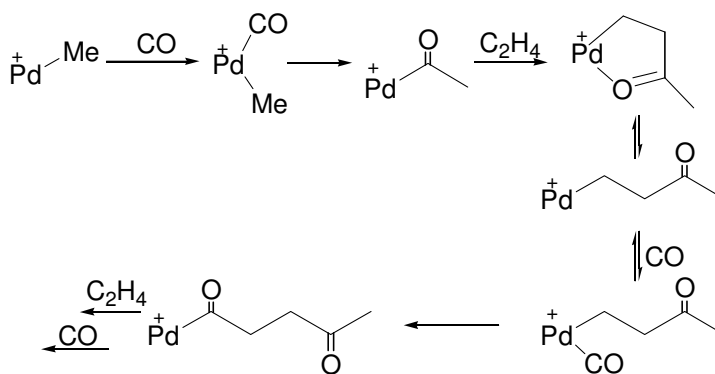
Scheme 1

To this purpose, palladium complexes stabilised by the two couples of ligands shown in **Figure 1,** *chapter 2*, section 2.1, pag. 67 were employed as model compounds.[5b,5c]

In situ high-pressure NMR (HP-NMR) and IR techniques have been employed to determine kinetic and thermodynamic parameters, while batch catalytic reactions in different experimental conditions have provided information on the dependence of the reaction rate on CO and ethene pressures. Incorporation of the results obtained unambiguously show that the *o*-methoxy groups can interact with the metal centre, leading to a mechanism where the opening of the β-keto chelates and the overall copolymerisation rate as well are zero-order with respect to the CO pressure.

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2.2.2. Results and Discussion

Generation of the β-Keto chelates [Pd(CH$_2$CH$_2$C(O)Me)(P-P)]BArF

The synthetic procedure to prepare the β-keto chelate complexes [Pd(CH$_2$CH$_2$C(O)Me)(P-P)]BArF (P-P = *o*-MeO-dppe, **3f**; *o*-MeO-dppp, **4f**; **(**ArF = 3,5-(CF$_3$)$_2$-C$_6$H$_3$) is illustrated in
Scheme 2.
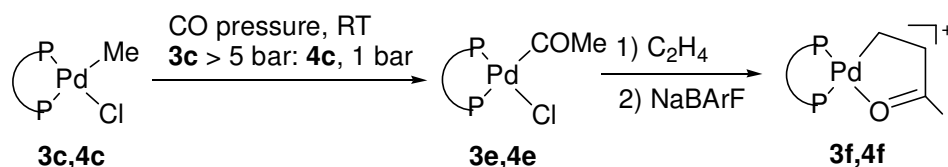
Scheme 2. *In situ* synthesis of palladium(II) β-Keto chelates **3f** and **4f**

The methyl chloride precursors PdCl(Me)(P-P) (P-P = *o*-MeO-dppe, **3c**; *o*-MeO-dppp, **4c**) were conveniently prepared by reaction of PdCl(Me)(COD) (COD = cycloocta-1,5-diene) with the appropriate diphosphine and isolated as off-white crystalline solids in 78% and 67% yield, respectively.[2d]

Unambiguous characterisation of **3c** and **4c** in solution was achieved by variable-temperature ^{1}H and ^{31}P{^{1}H} NMR spectroscopy in CD$_2$Cl$_2$ (*chapter 2*, section 2.1, pag. 102).[2d] Complexes **3c** and **4c** exhibit fluxional behavior on the NMR time-scale due to the exchange of equatorial and axial aryl groups. The ^{1}H NMR spectrum at 21 ^{o}C of either complex displayed one set of resonances for the aryl hydrogens (δ 6.87-7.91 and 6.87-7.58, respectively) and two singlets for the methoxy groups (δ 3.59/3.60 and 3.66/3.76, respectively),[2d] which is consistent with the presence of two couples of equivalent aryl groups in the *o*-MeO-ligands. Decreasing the temperature led to a progressive broadening of all resonances. At -70 ^{o}C, the ^{1}H NMR spectra of **3c** and **4c** showed four singlets

for the methoxy groups at δ 3.42, 3.44, 3.75, and 3.76 and δ 3.56, 3.67, 3.69, and 3.72, respectively. This pattern can be safely attributed to the formation of equatorially and axially oriented methoxy groups as illustrated in the sketch reported in **Figure 1**.[2d,6]
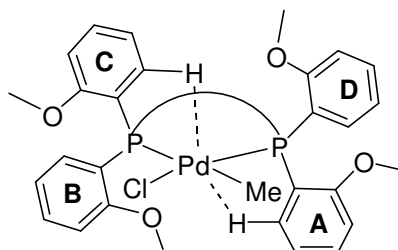

Figure 1. Low temperature conformation of **3c** and **4c**

The ^{1}H NMR spectra at -70 ^{o}C showed a significant downfield shift of the resonances of two aryl hydrogens (δ 8.450/8.61 and 8.55/8.8.74, respectively), which, on the basis of ^{1}H-^{31}P COSY experiments, can be assigned to the *o*-H atoms of the axial aryl rings **A** and **C** interacting with the metal centre. Analogous fluxional behavior has been previously reported for the X-ray authenticated complexes PdCl$_2$(P-P) (P-P = *o*-MeO-dppe, *o*-MeO-dppp).[2d] Further spectroscopic evidence in support of the conformation proposed in **Figure 1** was provided by a ^{1}H ROESY experiment at -70 ^{o}C of **3c**, indicating two significant correlations between the hydrogen atoms of the Pd methyl group and the *o*-H atoms of the aryl rings **A** and **D**. Based on this NMR study, it is highly probable that the slow-exchange conformation of PdCl(Me)(P-P) is stabilised by two *o*-methoxy oxygen atoms (from the equatorial aryl rings **B** and **D**) and by two *o*-H atoms (from the axial rings **A** and **C**), all pointing towards the palladium centre.

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A single-crystal X-ray analysis of **3c**·CHCl$_3$ has confirmed the structure proposed in solution. Suitable crystals were obtained by slow diffusion of toluene into a CHCl$_3$ solution of **3c**. An ORTEP drawing of **3c**·CHCl$_3$ is shown in **Figure 2**, while crystal data and selected distances and angles are reported in **Table 1** and **Table 2**, respectively.

Table 1. Crystal Data and Structure Refinement Details for **3c**·CHCl$_3$

Empirical formula	C$_{32}$H$_{36}$Cl$_4$O$_4$P$_2$Pd
Molecular mass [g mol^{-1}]	794.75
Crystal color, shape	white, plate
Crystal size [mm]	0.2 × 0.1 × 0.05
Temperature [K]	223
Crystal system	monoclinic
Space group	P2$_1$/c
a [Å]	9.294(6)
b [Å]	23.054(10)
c [Å]	22.295(11)
β [°]	94.75(5)
V [Å^3]	4761(4)
Z	4
Density (calculated), [g cm^{-3}]	1.109
F(000)	1616
θ range [°]	3.98-23.27
Radiation-wavelength [Å]	MoKα/0.71073
Absorption coefficient [mm^{-1}]	0.707
Reflections collected	18877
Independent reflections	6802
Data/restraints/parameters	5200/0/390
Gof on F^2	1.111
R1, wR2 ($I > 2\sigma(I)$)	0.1038, 0.2801
R1, wR2 (all data)	0.1190, 0.2970
Largest diff peak/hole [e Å^{-3}]	1.915/-2.054

Table 2. Selected Bond Length [Å] and Bond Angles [º] for **3c**·CHCl$_3$

Pd(1)-P(1)	2.221(2)
Pd(1)-P(2)	2.343(2)
Pd(1)-Cl(1)	2.389(2)
Pd(1)-C(31)	2.095(8)
P(1)-Pd(1)-P(2)	86.27(9)
C(31)-Pd(1)-Cl(1)	89.30(20)
Intramolecular Distances [Å]	
Pd(1)-O(1)	3.573(6)
Pd(1)-O(2)	5.181(6)
Pd(1)-O(3)	5.271(7)
Pd(1)-O(4)	3.870(6)
Pd(1)-H(9)	2.809
Pd(1)-H(16)	2.855
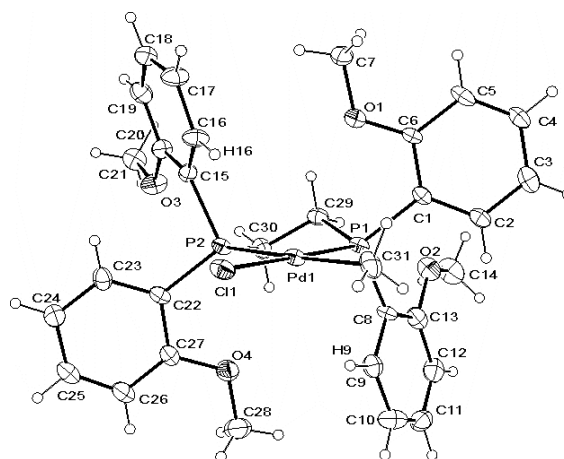
Figure 2. ORTEP plot of **3c**·CHCl$_3$. The solvent molecule was omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

The crystal structure shows a square-planar palladium centre coordinated by *cis* phosphorus atoms. The Pd-P bond lengths of 2.221(2) Å (*trans* to chloride) and 2.343(2) Å (*trans* to methyl) are in line with the greater *trans*-influence of the methyl group as compared to chloride. The four *o*-methoxy oxygen atoms are

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arranged around the palladium centre in such a way that two of them, O(1) and O(4), occupy a *pseudo*-apical position of the metal coordination sphere (Pd…O distances of 3.573(6) and 3.870(6) Å), while the other two, O(2) and O(3), are close to pseudo-equatorial positions (Pd…O distances of 5.181(6) and 5.271(7) Å). All of these Pd…O distances are too large for an effective electrostatic interaction between palladium and the *o*-methoxy groups. In contrast, the *o*-H atoms H(9) and H(16) show short intramolecular Pd…H distances of 2.809 and 2.855 Å, respectively, which are comparable to those found in the crystal structure of $PdCl_2$(*o*-MeO-dppe).[2d]

Pressurising a CH_2Cl_2 solution of **3c** with >5 bar CO in a 10 mm-OD HP-NMR tube at room temperature led to the immediate formation of the acetyl complex PdCl(COMe)(*o*-MeO-dppe) (**3e**). In contrast, the formation of the complex PdCl(COMe)(*o*-MeO-dppp) (**4e**) from **4c** required no pressurisation as it was quantitatively obtained by bubbling CO into a CH_2Cl_2 solution of the methyl complex at room temperature (**Scheme 2**). Once formed, the acetyl complexes were stable in solution even in the absence of CO. Ethene bubbling into CH_2Cl_2 solutions of the acyl complexes **3e** and **4e** for 2 min, followed by the addition of stoichiometric NaBArF, gave the β-keto chelates **3f** and **4f** (**Scheme 2**). Compounds **3e**, **3f, 4e,** and **4f** have been unambiguously characterised by variable-temperature $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. Selected NMR data are reported in **Table 3** and **Table 4**, respectively.

Table 3. $^{31}P\{^1H\}$NMR chemical shifts in ppm, (multiplicity), and [PP coupling constant in (Hz)] for the palladium complexes $[Pd(X)(Y)(P-P)]^{0/+}$ in CD_2Cl_2 solutions at {T in (^{o}C)}

P-P	X= COMe Y= Cl	X= (CH₂)₂COMe Y= (CH₂)₂COMe	X= (CH₂)₂COMe Y= CO	X= CO(CH₂)₂COMe Y= CO
o-MeO-dppe	37.50(d) [48.7] 27.80(d) **{22}**	58.00(d) [26.0] 26.77(d) **{-50}**	57.55(d) [29.5] 25.80(d) **{-50}**	36.02(d) [49.6] 16.74(d) **{-30}**
o-MeO-dppp	15.40(d) [75.9] -3.20(d) **{22}**	33.90(d) [57.6] -12.00(br.s)**{-90}**	21.30(d) [67.1] -30.50(br s) **{-90}**	8.86(d) [86.9] -29.16(d) **{-30}**

Table 4. ^1H NMR chemical shifts in ppm, (multiplicity) for the palladium complexes $[Pd(X)(Y)(P-P)]^{0/+}$ in CD_2Cl_2 solutions at {T in (^{o}C)}

P-P	X= COMe Y= Cl	X= (CH₂)₂COMe Y= (CH₂)₂COMe	X= (CH₂)₂COMe Y= CO	X= CO(CH₂)₂COMe Y= CO
o-MeO-dppe	1.79(s) CO*Me***{22}**	0.82(br m) PdC*H₂* 2.40(s) CO*Me* 3.13(m) C*H₂*COMe**{-50}**	0.30(br m) PdC*H₂* 2.10(s) CO*Me* 2.65(m) C*H₂*COMe**{-50}**	1.88(s) CO*Me* 3.10(m) C*H₂*COMe 2.25(m) PdCOC*H₂* **{-30}**
o-MeO-dppp	1.73(s) CO*Me***{22}**	0.84(br m) PdC*H₂* 2.17(s) CO*Me* 2.89(m)C*H₂*COMe**{-90}**	0.37(br m) PdC*H₂* 1.51(s) CO*Me* 2.42(m) C*H₂*COMe**{-90}**	1.92(s) CO*Me* 2.52(m) C*H₂*COMe 2.08(m) PdCOC*H₂* **{-30}**

Like the methyl chloride precursors **3c** and **4c**, the β-keto chelates **3f** and **4f** exhibit fluxional behavior in CD_2Cl_2 solution at room temperature, due to the exchange of equatorial and axial aryl groups. At -70 ^{o}C both compounds adopt the conformation shown in **Figure 3**.

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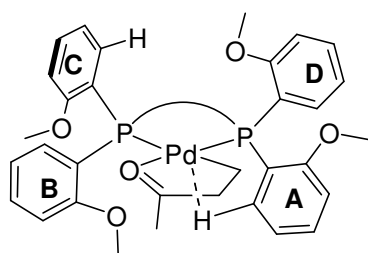**Figure 3.** Low temperature conformation of **3f** and **4f**

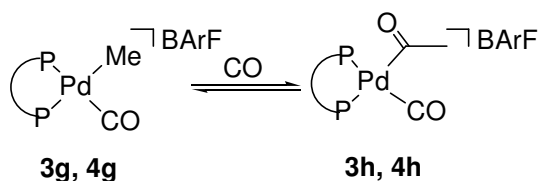The ^{1}H NMR spectra of **3f** and **4f** at -70 ^{o}C showed a multiplet at δ 8.48 and 8.28, respectively, which, on the basis of ^{1}H-^{31}P COSY experiments, was assigned to the *o*-H atom of ring **A**. At the same temperature, a [1]H-ROESY experiment of **3f** revealed the existence of significant correlations between the Pd-CH$_2$ unit and the *o*-H atoms of the aryl rings **A** and **D** and between the *o*-methoxy hydrogen atoms from the equatorial aryl ring **B** and the hydrogen atoms of the COMe unit. The stereochemical position of the aryl ring **C** could not be unambiguously determined, yet, due to the lack of the down-field shifted multiplet of the *o*-H atom of ring **C** in the ^{1}H NMR spectrum. It is very likely that ring **C** is turned around in such a way that the corresponding *o*-methoxy group points towards the metal centre. The β-keto chelates **3f** and **4f** and the corresponding derivatives with dppe (**1f**) and dppp (**2f**) were also characterised by *in situ* IR spectroscopy in CH$_2$Cl$_2$ at room temperature (**Table 5**). The spectra were scarcely informative except for showing a blue shift of ca. 6 cm^{-1} of the C=O stretching band for the *o*-methoxy-susbstituted complexes, which is consistent with the higher σ-donor ability of *o*-MeO-dppe and *o*-MeO-dppp as compared to dppe and dppp.

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Table 5. Selected IR absorption bands in CH_2Cl_2 of selected complexes

(P-P)	[Pd(CH$_2$CH$_2$C(O)Me)(P-P)]BArF ν(C=O)(cm^{-1})	[Pd(CO)(COMe)(P-P)]BArF ν(CO)/ν(C=O) (cm^{-1})
o-MeO-dppe	1636	2122/1696
dppe	1629	2130/1693
o-MeO-dppp	1636	2122/1700
dppp	1630	2129/1694

Generation and migratory insertion barriers of [PdMe(CO)(P-P)]BArF

The methyl carbonyl complexes [PdMe(CO)(P-P)]BArF (P-P = *o*-MeO-dppe, **3g**; *o*-MeO-dppp, **4g**) were selectively generated *in situ* by bubbling CO into a HP-NMR tube containing a CD$_2$Cl$_2$ solution of the corresponding chloride methyl complex at -100 ^{o}C. The kinetics of conversion of the methyl carbonyl complexes to the acetyl carbonyl products [Pd(CO)(COMe)(P-P)]BArF (P-P = *o*-MeO-dppe, **3h**; *o*-MeO-dppp, **4h**) (**Scheme 3**) were conveniently followed by variable-temperature ^{31}P{^{1}H} NMR spectroscopy in CD$_2$Cl$_2$. ^{31}P{^{1}H} and ^{1}H NMR data for **3g, 4g, 3h** and **4h** are given in **Table 6** and **Table 7**, respectively.

Scheme 3. Migratory insertion of **3g** and **4g**

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Table 6. $^{31}P\{^{1}H\}$ NMR chemical shifts in ppm, (multiplicity), and [PP coupling constant in Hz] for the palladium complexes [Pd(**X**)(**Y**)(P-P)]BArF in CD$_2$Cl$_2$ solutions at {T in ^{o}C}.

P-P	X= Me,Y= CO	X= COMe, Y= CO
o-MeO-dppe	57.59(d) [31.0]	35.75(d) [48.7]
	24.34(d) **{-50}**	16.55(d) **{-40}**
o-MeO-dppp	22.40(d) [62.8]	8.00(d) [88.7]
	-29.9(br s) **{-90}**	-28.5(d) **{-40}**

Table 7. ^{1}H NMR chemical shifts in ppm and (multiplicity) for the palladium complexes [Pd(**X**)(**Y**)(P-P)]BArF in CD$_2$Cl$_2$ solutions at {T in ^{o}C}.

P-P	X= Me, Y= CO	X= COMe, Y= CO
o-MeO-dppe	0.43(m) **{-50}**	1.65(s)**{-40}**
o-MeO-dppp	0.08(m) **{-90}**	1.88(s)**{-40}**

Consistent with the greater σ-donor ability of *o*-MeO-dppe and *o*-MeO-dppp vs. dppe and dppp, the IR spectra of the carbonyl acyl complexes **3h** and **4h** in CH$_2$Cl$_2$ (**Table 5**) showed a blue shift of the COMe absorption band (3-6 cm^{-1}) and a red shift of the CO absorption band (7-8 cm^{-1}) as compared to the analogue derivatives [Pd(CO)(COMe)(P-P)]BArF with dppe (**1h**) and dppp (**2h**).[2b,2c]

The study of the migratory insertion of the methyl(carbonyl) complexes was carried out at different CO pressures (5-20 bar), showing the reaction rate to be independent of the CO concentration. According to first-order kinetics, the free energy of activation for the migration insertion process was calculated applying the equation: $\Delta G^{\ddagger} = RT(\ln kT/h - \ln k_r)$ with $k_r = \ln2/t_{1/2}$ (T = temperature during the conversion; $t_{1/2}$ = half-life time in sec).[2b,2c] The values of the activation energies for the migratory insertion in **3g** and **4g** are given in **Table 8** that also reports data previously reported for the dppe and dppp analogues [PdMe(CO)(P-P)]BArF (P-P = dppe, **1g**; dppp, **2g**).[2b,2c]

**Table 8.** Experimental activation barriers and temperatures for migratory insertions.

L = P-P	[Pd(Me)(CO)(L)]$^+$			[Pd(CH$_2$CH$_2$C(O)Me)(L)]$^+$		[Pd(CH$_2$CH$_2$C(O)Me)(CO)(L)]$^+$			
	T (°C)	$t_{1/2}$ (min)	$\Delta G^{\ddagger}$ (kcal/mol)	T (°C)	$t_{1/2}$ (min)	p(CO) (bar)	T (°C)	$t_{1/2}$ (min)	$\Delta G^{\ddagger}$ (kcal/mol)
o-MeO-dppe	-40	52	17.4(1)	-60	25	20	-40	100	17.7(1)
dppe[2b]	-40	12	16.9(1)	-20	15	20			
o-MeO-dppp	-80	105	14.6(1)	-90	6	20	-60	10	15.2(1)
dppp[2c]	-60	10	15.2(1)	-70	84	20			

The results obtained showed the migratory insertion of PdMe(CO) to be a low-energy process for all complexes, yet lower for the dppp complexes than for the dppe ones and, in particular, for the o-MeO-dppp complex **4g**, which is known to generate most active catalysts in several reaction media.[2d]

Carbonylation reactions of the β-Keto chelates

The reactions of the β-keto chelates **3f** and **4f** with 20 bar CO in CD$_2$Cl$_2$ were studied *in situ* by ^{1}H and ^{31}P{^{1}H} HPNMR spectroscopy at low temperature. HP-NMR tubes containing CD$_2$Cl$_2$ solutions of these complexes under nitrogen were cooled to ca. -100 °C, pressurised with 20 bar CO and then inserted into the NMR probe-head pre-cooled at -90 °C. The conversion of the β-keto chelates into the carbonyl acyl complexes [Pd(CO)(COCH$_2$CH$_2$C(O)Me)(P-P)]BArF (P-P = o-MeO-dppe, **3j**; o-MeO-dppp, **4j**) was found to involve alkyl carbonyl intermediates of the formula [Pd(CO)(CH$_2$CH$_2$C(O)Me)(P-P)]BArF (P-P = o-MeO-dppe, **3i**; o-MeO-dppp, **4i**) (**Scheme 4**). Selected ^{31}P{^{1}H} and ^{1}H NMR data of final products and intermediates are reported in **Table 3** and **Table 4**, respectively, while sequences of ^{31}P{^{1}H} NMR spectra acquired during the

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carbonylation of either **3f** or **4f** with 20 bar CO are reported in **Figure 4** and **Figure 5**, respectively.
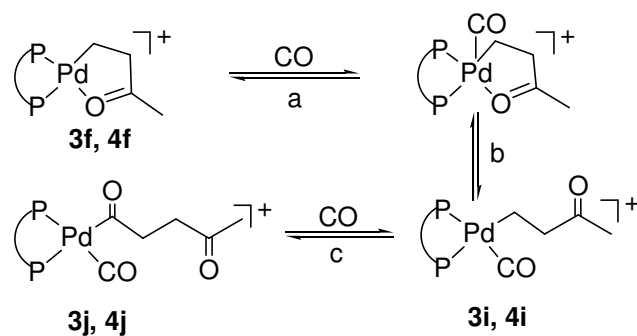
Scheme 4. Carbonylation of **3f** and **4f**

Compound **3f** started to convert into the alkyl carbonyl complex **3i** at -60 ^{o}C with a $t_{1/2}$ value of 25 min (**Figure 4**, trace **b**). Increasing the temperature to -40 ^{o}C led to the quantitative formation of **3i** already after recording the first ^{31}P$\{^{1}$H$\}$ NMR spectrum (trace **c**). At this temperature, **3i** slowly converted into the acyl carbonyl complex **3j** (trace **d**), which was the only phosphorus-containing species at room temperature (trace **e**).
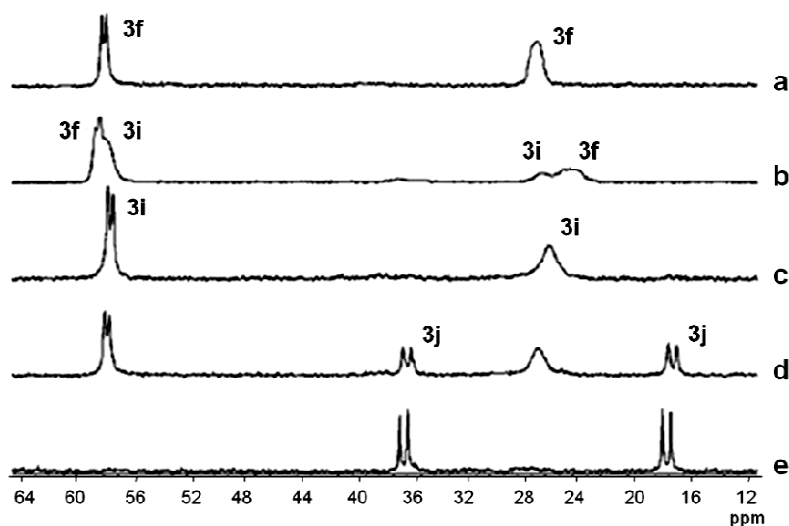
Figure 4. Variable-temperature $^{31}P\{^1H\}$ NMR study (sapphire tube, CD_2Cl_2, 81.01 MHz) of the carbonylation reaction of **3f**: (**a**) under nitrogen at -90 ^{o}C; (**b**) under CO (20 bar) after 40 minutes at -60 ^{o}C; (**c**) after 5 minutes at -40 ^{o}C; (**d**) after 80 minutes at -40 ^{o}C; (**e**) at room temperature

In an analogous experiment, **4f** was found to convert already at -90 ^{o}C into the alkyl carbonyl complex **4i** (**Figure 5**, trace **b**), which, in turn, started to transform into the final acyl carbonyl product **4j** (**Scheme 4**) at -80 ^{o}C. Due to the slow conversion rate at this temperature, the migratory insertion of **4i** was more conveniently evaluated at -60 ^{o}C (trace **d**).

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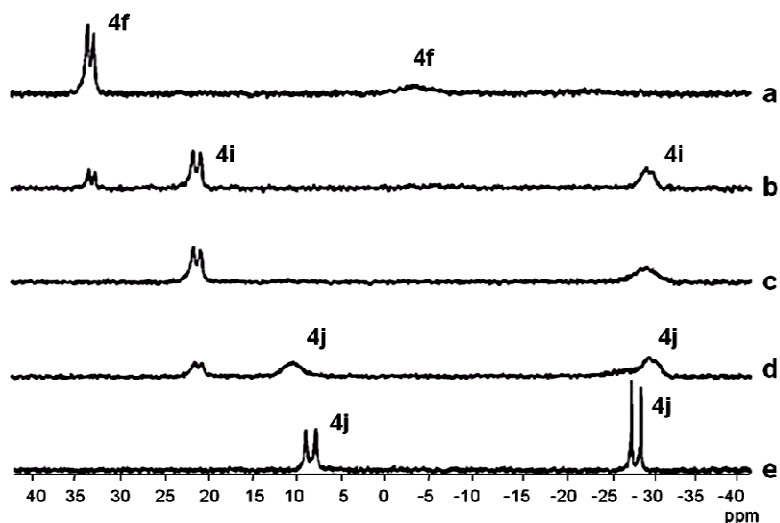**Figure 5.** Variable-temperature $^{31}P\{^1H\}$ NMR study (sapphire tube, CD_2Cl_2, 81.01 MHz) of the carbonylation reaction of **4f**: (**a**) under nitrogen at -90 ^{o}C; (**b**) under CO (20 bar) after 30 min at -90 ^{o}C; (**c**) after 30 min at -80 ^{o}C; (**d**) after 10 min at -60 ^{o}C; (**e**) at room temperature

To the best of our knowledge, so far alkyl carbonyl compounds such as **3i** and **4i** have never been intercepted along the carbonylation of diphosphine-modified palladium alkyl complexes. For the other new products obtained *in situ*, unambiguous characterisation of the alkyl carbonyl complexes was achieved by NMR spectroscopy as well as by comparison with the spectra of similar or related complexes (i.e., γ-keto acyl chelates)[7] described in the literature (**Table 3** and **Table 4**). Experimental evidence supporting the alkyl carbonyl structure of **3i** and **4i** was provided by the ^{31}P chemical shifts and the $^2J_{PP}$ coupling constants that were practically identical to those of the methyl carbonyl complexes **3g** and **4g**. Moreover, the ^1H NMR shifts of the $PdCH_2CH_2C(O)Me$ units were significantly upfield shifted with respect to the values observed for the β-keto chelates (**3f** vs **3i**: $C(O)CH_3$, δ 2.40 vs 2.10; $PdCH_2$, δ 0.82 vs 0.30. **4f** vs **4i**: $C(O)CH_3$, δ 2.17 vs 1.51; $PdCH_2$, δ 0.84 vs 0.37). In particular, the high-

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field shift of the C(O)Me singlets agrees well with the de-coordination of the carbonyl-oxygen atom from the metal centre.[7g]

Temperatures and $t_{1/2}$ values for the conversion of the β-keto-chelates **3f** and **4f** into the corresponding alkyl carbonyl product and the activation energies of the migratory insertions of the latter compounds are reported in **Table 8**. The opening of the β-keto-chelate ring by CO is apparently easier for the o-MeO-susbstituted complexes than for the PPh$_2$-ones, which might well account for the greater catalytic activity of the former complexes in batch reactions.[2d,3,4,5]

On the basis of these data, one may safely conclude that the alkyl migration to CO (step **c** of **Scheme 4**) limits the rate of carbonylation of the β-keto-chelates **3f** and **4f**, which is a relevant step in the propagation mechanism of the CO/ethene copolymerisation by palladium(II)-diphoshine catalysis.[1] Accordingly, since the Pd(CO)alkyl migratory insertion is independent of the CO pressure, the overall copolymerisation process would be independent of the CO pressure, at least under a gas pressure of 20 bar. This result dramatically differs from the previously reported studies of CO/ethene copolymerisation by the PPh$_2$-precursors **1f** and **2f** where the actual copolymerisation rate depends on both CO and C$_2$H$_4$ pressure[8] and the opening of the β-keto-chelates by CO is the rate limiting step in the propagation step involving CO insertion (**Table 8**).[2b,2c]

Catalytic CO/ethene copolymerisation reactions

In an attempt of determining the dependence of the copolymerisation rate on CO and ethene pressures in actual catalytic conditions, several batch reactions were carried out using either the o-MeO-modified chloride methyl complex **4c** or the analogous dppp derivative **2c** in CH$_2$Cl$_2$ at 50 °C.[2d] The results of this study are summarised in **Table 9** that also reports data obtained in MeOH with the known catalyst [Pd(H$_2$O)$_2$(o-MeO-dppp)](OTs)$_2$.[2d] In excellent accord with the

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present kinetic study, the catalytic activity of **4c** did not vary with the CO pressure in the range from 5 to 30 bar (entries 1,2,4), whereas an increase in activity occurred on increasing the C_2H_4 pressure (entry 3 vs. 2). In contrast, the productivity of the dppp precursor **2c** showed a clear dependence on the CO pressure (entries 5-6), which is in accord with a previous kinetic study by Toniolo and Chaudhari for reactions carried out in MeOH.[8] The latter solvent was therefore used in reactions catalysed by the [Pd$(H_2O)_2$(o-MeO-dppp)]$(OTs)_2$[2d] precursor (entries 7-9) that showed no dependence on the CO pressure above 10 bar, thus confirming and generalising the results of the present kinetic study in CH_2Cl_2. Noteworthy, a zero-order dependence on the CO pressure has been also reported for the CO/ethene/propene terpolymerisation catalysed by the water-soluble system palladium acetate/sulfonated o-MeO-dppp.[9]

Table 9. Ethene/CO copolymerisation reactions catalysed by palladium diphosphine precursors in different solvents

Entry[a]	Precursor	P(CO)	P(C_2H_4)	Productivity[b]
1	PdCl(Me)(o-MeO-dppp)	5	20	5.0
2	PdCl(Me)(o-MeO-dppp)	20	20	5.1
3	PdCl(Me)(o-MeO-dppp)	20	40	7.4
4	PdCl(Me)(o-MeO-dppp)	30	20	4.9
5	PdCl(Me)(dppp)	5	20	0.6
6	PdCl(Me)(dppp)	20	20	2.8
7[c]	[Pd$(H_2O)_2$(o-MeO-dppp)]$(OTs)_2$	10	20	17.0
8[c]	[Pd$(H_2O)_2$(o-MeO-dppp)]$(OTs)_2$	15	20	16.8
9[c]	[Pd$(H_2O)_2$(o-MeO-dppp)]$(OTs)_2$	20	20	18.1

[a]Reaction conditions: precursor (0.010 mmol), CH_2Cl_2 (75 ml), NaBArF (1.5 equiv.), BQ (80 equiv.), 20 min., 50 °C, 1200 rpm; [b]Productivity: kg alt-E-CO (g Pd x h)$^{-1}$; [c]Reaction conditions: precursor (0.0024 mmol), MeOH (100 ml), 1 h, 85 °C, 1200 rpm.

2.2.3. Conclusions

In situ high-pressure NMR studies supported by batch catalytic reactions have unambiguously shown that the presence of *o*-MeO substituents on the P-aryl rings affects the kinetics of the CO/ethene copolymerisation by palladium(II)-chelating diphosphine catalysis. Unlike analogous catalysts without *o*-methoxy-substituted ligands, the rate of carbonylation of the β-keto chelates is limited by the palladium(alkyl)(CO) migratory insertion, which makes the overall copolymerisation process independent of the CO pressure, at least in the range of the partial CO pressures investigated (5-30 bar).

No direct evidence for the coordination of the *o*-MeO group to palladium has been observed in the course of either migratory insertion or carbonylation reactions, yet NMR spectroscopy shows the aryl rings to adopt a conformation which favors the interaction between the *o*-MeO oxygen atoms and the metal centre.

2.2.4. Experimental Section

General Procedures

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. PdCl(Me)(COD)[10], [PdCl(Me)(P-P)] ((P-P) = *o*-MeO-dppe (**3c**), *o*-MeO-dppp (**4c**))[2d], [Pd(CH$_2$CH$_2$C(O)Me)(dppe)]BArF (**1f**),[2b] (COD = cycloocta-1,5-diene; BArF = tetrakis 3,5-bis(trifluoromethyl)phenyl borate), [Pd(CH$_2$CH$_2$C(O)Me)(dppp)]BArF (**2f**),[2c] [Pd(CO)(C(O)Me)(dppe)]BArF (**1h**),[2b] [Pd(CO)(C(O)Me)(dppp)]BArF (**2h**)[2c] and NaBArF[11] 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. Copolymerisation reactions were performed with a 250 mL stainless steel autoclave, constructed at the ICCOM-CNR (Florence, Italy), equipped with a magnetic drive stirrer and a Parr 4842 temperature and pressure controller. The autoclave was connected to a gas reservoir to maintain a constant pressure during the catalytic reactions. GC/MS analyses of the solutions were performed on a Shimadzu QP2100S apparatus equipped with a SPB-1 Supelco fused silica capillary column (30m, 0.25 mm i.d., 0.25μm film thickness). Deuterated solvents for routine NMR measurements were dried over molecular sieves. ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ 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 (^{1}H and ^{13}C NMR) or 85% H_3PO_4 (^{31}P NMR). ^{1}H-^{31}P COSY spectra and ^{1}H ROESY were recorded on a Bruker Avance DRX-400 spectrometer. High pressure NMR experiments were carried out on Bruker ACP 200 using a 10mm sapphire NMR tube, which was purchased from Saphikon (Milford, NH), while the titanium high-pressure charging head was constructed at the ISSECC-CNR (Florence-Italy).[12] Elemental analyses were performed using a Carlo Erba Model 1106 elemental analyser. Infrared spectra were recorded on a FT-IR Spectrum GX instrument (Perkin Elmer).

Syntheses

In situ Synthesis of the acetyl chloride complexes PdCl(COMe)(P-P)

In a typical experiment, a solid sample of the methyl chloride complex PdCl(Me)(P-P) (0.03 mmol) was dissolved in a Schlenk tube containing CD_2Cl_2 (2 mL) under nitrogen at room temperature. The resulting solution was first transferred into a 10 mm sapphire tube and then pressurised to >5 bar of CO at room temperature. Irrespective of the diphosphine the quantitative formation of the corresponding acetyl chloride complex PdCl(COMe)(P-P) (P-P = *o*-MeO-dppe, **3e**; *o*-MeO-dppp, **4e**). occurred at room temperature. The most relevant $^{31}P\{^1H\}$ and ^1H NMR chemical shifts and coupling constants for **3e** and **4e** are reported in **Table 3** and **Table 4**, respectively. The excess CO was released and nitrogen was gently bubbled through the solution previously cooled to -30 ^{o}C for 2 min to eliminate any trace of CO. Both complexes were found to be stable also in the absence of CO. Unlike **3e**, **4e** was generated even by bubbling CO through **4c** solutions for 5 minutes at room temperature. A procedure analogous to that described above was applied to prepare CH_2Cl_2 solutions of **3e** and **4e** for the IR characterisation: ν(C=O) 1669 cm^{-1} (**3e**), 1674 cm^{-1} (**4e**)

In situ Synthesis of the β-Keto chelates [Pd(CH$_2$CH$_2$C(O)Me)(P-P)]BArF

In a typical experiment, a solution of PdCl(COMe)(P-P) (0.03 mmol) in CD_2Cl_2 (2 mL) was prepared as above in a Schlenk tube at -30 ^{o}C under nitrogen. Ethene was bubbled through the solution maintained at -30 ^{o}C for 2 min and then a solid sample of NaBArF (26,59 mg, 0.03 mmol) was added to the solution to scavenge the chloride ligand from Pd. The resulting solution was transferred into a 10 mm sapphire tube. $^{31}P\{^1H\}$ and ^1H NMR spectra were acquired in the temperature range from 20 to -90 ^{o}C. Irrespective of the

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diphosphine ligand, the $^{31}P\{^1H\}$ and ^1H NMR spectra of this sample showed the quantitative conversion of the chloride acyl complex into the corresponding β-keto chelate complex $[Pd(CH_2CH_2C(O)Me)(P-P)]BArF$ (P-P = o-MeO-dppe, **3f**; o-MeO-dppp, **4f**). IR spectra of **3f** and **4f** were acquired from CH_2Cl_2 solutions of these compounds prepared by applying the same synthetic protocol as described above, using CH_2Cl_2 instead of CD_2Cl_2. The IR values of the CO stretching frequencies are reported in **Table 5**.

Compound 3c: $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_2Cl_2, -70 °C) 57.36 (d, $^2J_{PP}$ = 26.9 Hz, P_A), 25.43 (br, P_M); ^1H NMR (δ, 400.13 MHz, CD_2Cl_2, -70 °C) 0.82 (m, 1H, PdCH*H*), 1.21 (m, 1H, PdC*H*H), 2.05 (m, 2H, PC*H_2*), 2.42 (m, 3H, COC*H_3*), 2.58 (m, 2H, P'C*H_2*), 2.80 (m, 1H, COCH*H*), 3.08 (m, 4H, COC*H*H + OC*H_3*), 3.51 (s, 3H, OC*H_3*), 3.80 (s, 3H, OC*H_3*), 3.83 (s, 3H, OC*H_3*), 6.72-7.82 (m, 27H, Ar), 8.48 (dd, $^2J_{HP}$ = 17.0 Hz, $^3J_{HH}$ = 7.3 Hz, 1H, o-H-Ar$_{ax.}$(P_A))

Compound 4c: $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_2Cl_2, -70 °C) 33.51 (d, $^2J_{PP}$ = 57.9 Hz, P_A), -12.4 (br, P_M); ^1H NMR (δ, 400.13 MHz, CD_2Cl_2, -70 °C) 0.95 (m, 2H, PdC*H_2*), 2.21 (s, 3H, COC*H_3*), 2.31 (m, 3H, PC*H*H + C*H_2*), 2.51 (m, 2H, PCH*H* + P'C*H*H), 2.92 (m, 3H, COCH_2 + P'C*H*H), 3.59 (s, 3H, OC*H_3*), 3.70 (s, 3H, OC*H_3*), 3.83 (s, 3H, OC*H_3*), 3.86 (s, 3H, OC*H_3*), 6.62-7.83 (m, 27H, Ar), 8.28 (dd, $^2J_{HP}$ = 17.0 Hz, $^3J_{HH}$ = 7.1 Hz, 1H, o-H-Ar$_{ax.}$(P_A))

***In situ* generation and migratory insertion barriers of [PdMe(CO)(P-P)]BArF. HP-NMR experiments**

In a typical experiment, the methyl chloride complex PdCl(Me)(P-P) (0.03 mmol) was dissolved in deoxygenated CD_2Cl_2 (2 mL)and the resulting solution was then transferred into a 10 mm sapphire tube, which was cooled to -100 °C by means of an ethanol/liquid nitrogen bath. CO was bubbled through this solution for 2 min at this temperature, followed by the addition of NaBArF (26.59 mg, 0.03 mmol). The CO pressure was adjusted to the desired value (5-20 bar). The

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solution was shaken for 2 min at -100 $^{\circ}$C, followed by the introduction of the sapphire tube into the probe-head previously cooled to -90 $^{\circ}$C. Irrespective of the diphosphine ligand, the $^{31}P\{^1H\}$ and ^1H NMR spectra showed the quantitative conversion of the starting methyl chloride complex into the corresponding methyl carbonyl complexes [PdMe(CO)(P-P)]BArF (P-P = *o*-MeO-dppe, **3g**; *o*-MeO-dppp, **4g**) (selected $^{31}P\{^1H\}$ and ^1H NMR data of the methyl carbonyl complexes are reported in **Table 6** and **Table 7**, respectively). Afterwards the probe temperature was gradually increased and $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded at each intermediate temperature. Increasing the temperature converted each methyl carbonyl complex into the corresponding carbonyl acyl derivative [Pd(COMe)(CO)(P-P)]BArF (P-P= *o*-MeO-dppe, **3h**; *o*-MeO-dppp, **4h**) (selected $^{31}P\{^1H\}$ and ^1H NMR data of the carbonyl acyl complexes are reported in **Table 6** and **Table 7**, respectively). At the conversion temperature, the decrease in concentration of the methyl carbonyl complex was followed by $^{31}P\{^1H\}$ NMR spectroscopy. Spectra were taken at intervals of 5-10 min, depending on conditions. The reaction was followed for 2-3 half-lives. IR spectra of **3h** and **4h** were acquired from CH_2Cl_2 solutions of these compounds prepared by applying the same synthetic protocol as described above, using CH_2Cl_2 instead of CD_2Cl_2. The IR values of the CO stretching frequencies are reported in **Table 5**.

Carbonylation of the β-Keto chelates [Pd(CH$_2$CH$_2$C(O)Me)(P-P)]BArF. HP-NMR experiments

CD_2Cl_2 (2 mL) solutions of the β-keto chelates [Pd(CH$_2$CH$_2$C(O)Me)(P-P)]BArF (P-P = *o*-MeO-dppe, **3f**; *o*-MeO-dppp, **4f**) (0.03 mmol) were synthesised *in situ* in a Schlenk tube at -30 $^{\circ}$C, as described above. Nitrogen was bubbled through the solution to eliminate any trace of ethene. The solutions were transferred into a 10 mm sapphire tube at room temperature. Then the sapphire tube was introduced in a pre-cooled NMR probe (-90 $^{\circ}$C) and $^{31}P\{^1H\}$ and ^1H NMR

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spectra were acquired at this temperature. The sapphire tube was then removed from the probe and immersed into an ethanol/liquid nitrogen thermostat bath (ca. -100 ^{o}C) before to be charged with CO (5-20 bar). Afterwards the sapphire tube was introduced again into the NMR probe head at -90 ^{o}C. ^{31}P{^{1}H} and ^{1}H NMR spectra showed that the β-keto-chelate complexes were still present. Afterwards the probe temperature was gradually increased and ^{31}P{^{1}H} and ^{1}H NMR spectra were recorded at each intermediate temperature. Increasing the temperature caused the conversion of the β-keto-chelate complex into the corresponding carbonyl acyl derivative [Pd(CO)(COCH$_2$CH$_2$C(O)Me)(P-P)]BArF (P-P = o-MeO-dppe, **3j**; o-MeO-dppp, **4j**) *via* the alkyl carbonyl complexes [Pd(CO)(CH$_2$CH$_2$C(O)Me)(P-P)]BArF (P-P = o-MeO-dppe, **3i**; o-MeO-dppp, **4i**). Selected high pressure ^{31}P{^{1}H} NMR spectra of the carbonylation of either **3f** or **4f** under 20 bar of CO are shown in **Figure 4** and **Figure 5**, respectively. Selected ^{31}P{^{1}H} and ^{1}H NMR data of the complexes **3i**, **4i**, **3j**, and **4j** are reported in **Table 3** and **Table 4**, respectively. At the conversion temperature the decrease in concentration of the β-keto chelates was followed by ^{31}P{^{1}H} NMR spectroscopy. Spectra were taken at intervals of 5-10 min, depending on conditions. The reaction was followed for 2-3 half-lives.

[Pd(CH$_2$CH$_2$C(O)Me)(P-P)]BArF/[Pd(COCH$_2$CH$_2$C(O)Me)(CO)(P-P)]BArF equilibria

Solutions of the carbonyl acyl complexes **3j** and **4j,** prepared as reported above in HPNMR tubes, were immersed in a thermostat bath at -20 ^{o}C. CO was released and then couples of vacuum-nitrogen cycles were applied. ^{31}P{^{1}H} and ^{1}H NMR spectra of these samples acquired at -20 ^{o}C let us to follow the transformation of the carbonyl acyl complexes into the corresponding β-chelates **3f** and **4f**.

Catalytic copolymerisation reactions in CH$_2$Cl$_2$

CH$_2$Cl$_2$ (75 mL), saturated with CO at room temperature, was introduced by suction into an autoclave (250 mL), previously evacuated by a vacuum pump, containing the catalyst precursor (0.010 mmol) and NaBArF (0.012 mmol). The autoclave was charged with the required pressures of CO and C$_2$H$_4$ at room temperature and then heated. As soon as the temperature reached 50 ^{o}C, stirring (1200 rpm) was started and the catalytic reaction was conducted under constant pressure. After 20 min, the autoclave was cooled by means of an ice-water bath and the unreacted gases were released. The insoluble copolymer was filtered off, washed with CH$_2$Cl$_2$, and dried under vacuum at 60 ^{o}C to constant weight.

Catalytic copolymerisation reactions in MeOH

Typically, MeOH (100 mL), was introduced by suction into an autoclave (250 mL), previously evacuated by a vacuum pump, containing the catalyst precursor (0.0024 mmol) and 1,4-benzoquinone (BQ, 0.192 mmol). The autoclave was charged with the desired pressure of CO and C$_2$H$_4$ at room temperature and then heated. As soon as the temperature reached 85 ^{o}C, stirring (1200 rpm) was started and the catalytic reaction was conducted under constant pressure for 1 h. Afterwards the autoclave was cooled by means of an ice-water bath and the unreacted gases were released. The insoluble copolymer was was filtered off, washed with MeOH, and dried under vacuum at 60 ^{o}C to constant weight.

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Crystal structure determination of 3c·CHCl$_3$

Several crystallisation attempts with different solvents were performed and only by the diffusion of toluene into a CHCl$_3$ solution of **3c** gave single crystal, although of poor quality. X-ray diffraction intensity data were collected at 223 K on an Oxford Diffraction CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) using ω-scans. Cell refinement, data reduction and empirical absorption correction were carried out with the Oxford diffraction software and SADABS.[13a] All structure determination calculations were performed with the WINGX package[13b] with SIR-97,[13c] SHELXL-97[13d] and ORTEP-3 programs[13e] 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 depending on the Ueq of the adjacent carbon atoms.

Acknowledgments

2.2.5. References

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