Labeling studies of some carbonylation reactions of styrene with cationic palladium complexes

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Abstract

The dicarbonylation reaction of E-β-deuteriostyrene to syndiotactic poly(1-oxo-2-phenyltrimethylene) as well as to dimethyl-2-phenylbutanedioate and dimethyl-2,5-diphenyl-4-oxoheptanedioate using $Pd(CF_3COO)_2/2,2'$-bipyridine as the catalyst precursor in the presence of 1,4-benzoquinone in methanol takes place stereospecifically in a *syn*-fashion with complete retention of the label. The same result was found for the dicarbonylation to dimethyl 2-phenylbutanedioate catalyzed by $[Pd(CF_3COO)_2(Diop)]$. In the absence of the oxidant the latter catalytic system produces methyl 2- and 3-phenylpropionates for which some scrambling of deuterium is observed when using either α-deuteriostyrene or CH_3OD as the labeled substrate. $[Pd(CH_3CN)_4][BF_4]_2$ modified with different ligands catalyses the formation of E-1,5-diphenylpent-1-en-3-one or of E-1,4-diphenylpent-1-en-3-one in tetrahydrofuran as the solvent. The label distribution using E-β-deuteriostyrene as the substrate (or styrene in the presence of dideuterium) suggests that in the synthesis of ketones catalyzed by $[Pd(p\text{-}CH_3C_6H_4SO_3)_2(Dppp)] \cdot 2H_2O$ the regioselectivity of the first inserted olefin unit does not determine the ketone regioisomer; rather which regioisomeric product preferentially forms depends on the rate of carbon monoxide insertion in either the branched or linear metal–hydrocarbyl intermediate. β-Hydrogen elimination is very rapid both after the first and the second olefin insertion.

Key words: Carbonylation; Ketone; Succinate; Poly(1-oxo-2-phenyltrimethylene); Cationic palladium complexes

Introduction

Carbonylation reactions of olefinic substrates are of interest due to the nature of the different products that can be obtained [1]. Recent investigations on cationic palladium complexes have even broadened the scope of those reactions [2]. In fact new selective and stereoselective ways to ketones [3], polyketones [2b, 4] and succinic acid derivatives [5] have been found. These possibilities are shown in Scheme 1, in particular referring to styrene as the substrate for which all reactions described can be carried out with fair to high selectivities. Considering that the catalyst precursors and the reaction conditions for these reactions are quite similar, upon closer examination of the scheme the question arises which factors determine the selectivity and in particular which factors control the molecular weight of the products. Thus $[Pd(CH_3CN)_4][BF_4]_2$ modified with 1,10-phenanthroline or 1,3-propanediylbis(diphenylphosphine) catalyses at ~ 100 °C the stereoselective formation of E-1,5-diphenylpent-1-en-3-one in THF as the solvent [3a, b]. In the presence of hydrogen, 1,5-diphenylpentan-3-one is also formed. In this reaction apparently β-hydrogen elimination causes a break of the chain growth after the insertion of the second styrene unit [3b]. Under the same conditions the phenanthroline containing system in methanol as the solvent is able to catalyse the formation of low molecular weight syndiotactic poly(1-oxo-2-phenyltrimethylene) [6]. The presence of the two possible 2- and 1-phenylethyl end groups (the latter being prevalent) in addition to styryl end groups in these oligomers (ratio $\sim 0.9/1$) implies a chain initiation by a palladium–hydride species and termination through β-hydrogen elimination. Traces of dihydrogen shift the selectivity towards the formation of ketones. When an oxidant (such as 1,4-benzoquinone) is present the formation of syndiotactic poly(1-oxo-2-phenyltrimethylene) already takes place at temperatures close to ambient [4c, 7]. Under these conditions the macromolecular chains form through secondary insertions of the styrene units beginning with a palladium–carbomethoxy species [4d, k]. Again, termination

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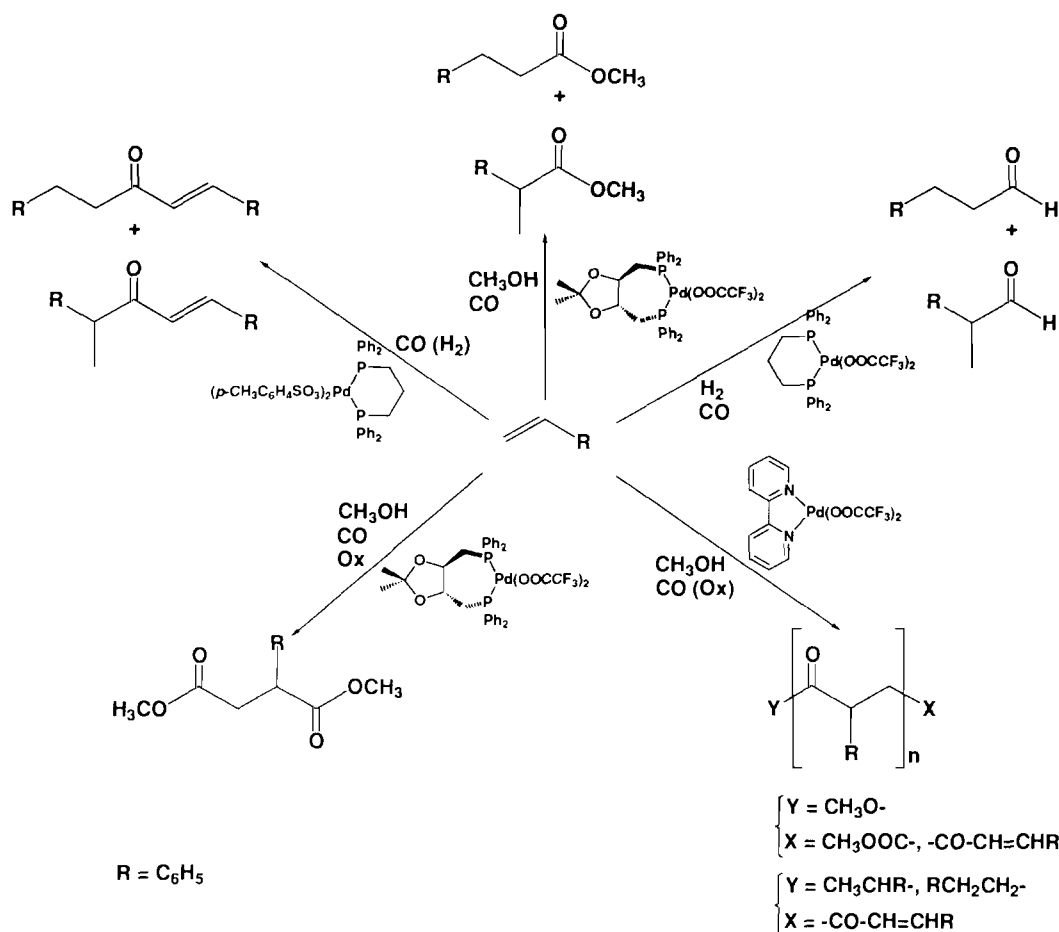
Scheme 1.

of the chain is caused mostly by β-hydrogen elimination leading to a styryl group; alternatively, alcoholysis of an acyl group leading to a carbomethoxy group can take place. In contrast to the aforementioned nitrogen ligands, diphosphine modified catalytic systems in methanol as the solvent led to hydrocarbomethoxylation as well as to bis-carbomethoxylation when 1,4-benzoquinone is present [8].

We report here on some studies mostly using labeled substrates concerning the synthesis of esters and diesters and of ketones and polyketones, in connection with the aforementioned problems of controlling product selectivity and molecular weight. Some preliminary results concerning the stereochemistry of the formation of succinates using E-β-deuteriostyrene as the substrate have already been presented in a short form [8].

Results and discussion

Carbonylation to oligomeric compounds

The dicarbonylation of E-β-deuteriostyrene (isotopic purity 91%) was carried out with an *in situ* catalytic

system consisting of $Pd(CF_3COO)_2/2,2'$-bipyridine in the presence of 1,4-benzoquinone and 1,4-hydroquinone, using methanol as the solvent [8]. Prevailingly syndiotactic poly(1-oxo-2-phenyltrimethylene) (65%, average polymerization degree ~ 10), dimethyl 2,5-diphenyl-4-oxoheptanedioate (7%) and dimethyl 2-phenylbutanedioate (16%) were isolated. NMR and MS analysis of dimethyl 2-phenylbutanedioate and dimethyl 2,5-diphenyl-4-oxoheptanedioate showed complete retention of the label and a clean *syn*-addition in the dicarbonylation reaction. No information was obtained from the NMR spectrum of poly(1-oxo-2-phenyltrimethylene) in hexafluoroisopropanol, which is normally used as the solvent for this material [4c, d, k]. In the meantime we have found [6] that the formed low molecular poly(1-oxo-2-phenyltrimethylene) obtained can be dissolved in chloroform. In this solvent, at variance with hexafluoroisopropanol, the two diastereotopic methylene protons are clearly separated in the ^{1}H NMR spectrum (Fig. 1). Exclusive labeling for the hydrogen atom at 2.60 ppm is recognised in the ^{2}H NMR spectrum, whereas complete retention of the label is inferred from the integration in the ^{1}H NMR
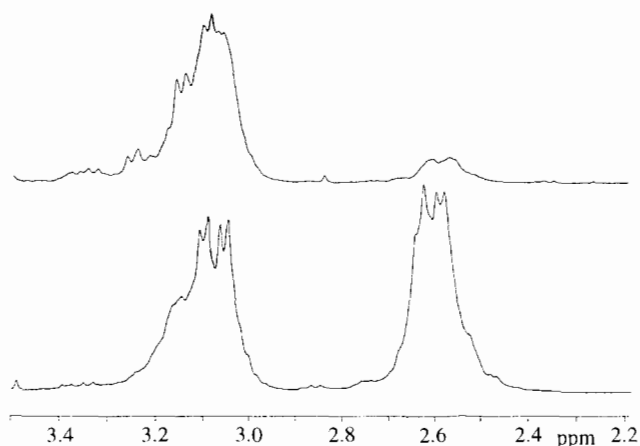
Fig. 1. Comparison of the ^{1}H NMR spectra (CDCl$_3$, 400 MHz) in the region of the diastereotopic methylene protons for poly(1-oxo-2-phenyltrimethylene) from styrene (lower spectrum) and *E*-β-deuteriostyrene (upper spectrum).

spectrum using the phenyl protons as the internal standard. In fact, the intensity of the residual signal at 2.60 ppm does correspond to the isotopic purity of the starting substrate. Furthermore, on the basis of the NMR data of model compounds [8] the *syn*-stereochemistry of the copolymerisation reaction is clearly demonstrated.

Carbonylation to polyketones and to ketones

A similar catalytic system formed from [Pd-(CH$_3$CN)$_4$][BF$_4$]$_2$/1,10-phenanthroline in methanol also catalyses the formation of syndiotactic poly(1-oxo-2-phenyltrimethylene) in the absence of the oxidant. Under these conditions higher temperatures ($\sim$100 °C) are required. The produced copolymer in this case shows 1-phenylethyl and 2-phenylethyl end groups in addition to styryl end groups. The branched end group largely prevails. In the presence of traces of hydrogen ketones (*infra vide*) are prevailingly formed; high pressure of dihydrogen causes complete reduction of the catalytic system to palladium metal. In tetrahydrofuran as the solvent the same system is only active under hydrogen pressure and causes highly selective formation of *E*-1,5-diphenylpent-1-en-3-one and 1,5-diphenyl-pentan-3-one [3b].

Carbonylation to ketones

The results obtained in the carbonylation of the same *E*-β-deuteriostyrene in the presence of diprotium to *E*-1,5-diphenylpent-1-en-3-one and to 1,5-diphenyl-pentan-3-one in THF at 100 °C using [Pd(*p*-CH$_3$C$_6$H$_4$SO$_3$)$_2$(Dppp)]·2H$_2$O (Dppp is 1,3-propane-diylbis(diphenylphosphine)) as the catalyst precursor are summarised in Table 1. In contrast to the aforementioned dicarbonylation reaction an extensive scrambling of the label (both inter- and intramolecular) takes

place in all cases. Furthermore loss of the label is apparent from the average number of the deuterium atoms per molecule. This loss takes place through scrambling between substrate and gas phase and between substrate and solvent, particularly if ketones are present. The former scrambling was revealed by the formation of a small amount of HD in the gas phase but not extensive enough to be exclusively responsible for the missing label. In the meantime it was found [9] that [Pd$_2$(μ-H)(μ-CO)(Dippp)$_2$]$^+$Cl$^-$ (Dippp is 1,3-propanediylbis(diisopropylphosphine)) is able to catalyse the scrambling of hydrogen between deuterated ketones and olefins and that this scrambling is limited to the α-position with respect to the carbonyl group. A similar binuclear palladium complex could form under carbonylation conditions from the precursors used in our study (i.e. with dppp as the ligand) [10], possibly through the intermediate formation of [Pd(μ-OH)(dppp)]$_2$[X$_2$] [3a] due to the presence of traces of water. In fact, traces of acetone in the solvent used (acetone was employed to clean the autoclave) were found by ^{1}H and ^{2}H NMR spectroscopy to be deuterated. It is to be noted that scrambling with ketones could also involve the formed *E*-1,5-diphenylpent-1-en-3-one at position 4 and 1,5-diphenylpentan-3-one at positions 2 and 4.

Considerable amounts of deuterium were found in positions at which no label would be expected, i.e. positions 5 and 1 in *E*-1,5-diphenylpent-1-en-3-one and 5 in 1,5-diphenylpentan-3-one arising from the carbonylation of *E*-β-deuteriostyrene. This as well as the formation of products containing more than two deuterium atoms can be interpreted on the basis of a rapid reversibility of the insertion of styrene in a palladium–hydride species. Based on this assumption the regioselective formation of the linear ketones with the catalyst precursor used is a consequence of a more rapid carbon monoxide insertion into a metal–primary-alkyl than in a metal–secondary-alkyl intermediate*. β-Hydrogen elimination from the alkyl species arising from the insertion of the second styrene unit is responsible for the selective formation of the unsaturated straight chain ketone (Scheme 2). The aforementioned label distribution can thus be accounted for as follows. Palladium–deuteride and unlabeled styrene can be formed from the facile β-deuterium elimination from a secondary alkyl–metal intermediate resulting from the insertion of *E*-β-deuteriostyrene into a palladium–hydride bond. The primary insertion of either the unlabeled styrene or labeled styrene into this palladium–deuteride bond followed by rapid insertion of carbon monoxide into the palladium–alkyl bond of this

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*For similar results in the rhodium catalysed hydroformylation of styrene see ref. 11.

TABLE 1. Intra- and intermolecular deuterium distribution (%) in the ketones obtained in the carbonylation of styrene

	MDN^a	d_0	d_1	d_2	d_3	MDN^b
Ph—CH₂——CH₂—CO—CH═CH—Ph						
(A) 0.63 0.12 0.55 0.10	1.40	22	40	30	8	1.22
(B) 0.04 0.16 0.00 0.00	0.20	79	21			0.21
Ph—CH₂——CH₂)₂ CO						
(A) 0.50 0.70	1.20	20	44	31	5	1.20
(B) 0.10 0.20	0.30	76	21	3		0.27
Ph—CH——CH₃CO—CH═CH—Ph						
(C) 0.07 0.15 0.05 0.00	0.27	nd	nd	nd	nd	nd

(A) Carbonylation of E-β-deuteriostyrene: [Pd(p-CH$_3$C$_6$H$_4$SO$_3$)$_2$(Dppp)]·2H$_2$O (0.07 mmol) as the catalyst precursor; styrene 11.2 mmol, THF 10 ml; 100 °C; p(CO) 20 bar; p(H$_2$) 1 bar; 20 h; yield 85%; sat/uns=46/52.
(B) Carbonylation of styrene: [Pd(p-CH$_3$C$_6$H$_4$SO$_3$)$_2$(Dppp)]·2H$_2$O (0.45 mmol) as the catalyst precursor; styrene 74 mmol, THF 25 ml; 100 °C; p(CO) 20 bar; p(D$_2$) 2 bar; 2 h; yield 94%; sat/uns=15/82.
(C) Carbonylation of styrene [Pd(CH$_3$CN)$_4$][BF$_4$]$_2$/(C$_6$H$_5$)$_2$PCH$_2$CH$_2$SC$_2$H$_5$ (0.50/0.50 mmol) as the catalyst precursor; styrene 56.5 mmol, THF 25 ml; 105 °C; p(CO) 80 bar; p(D$_2$) 80 bar; 20 h; yield 23%; sat/uns=2/92.
MDN=average number of deuterium atoms per molecule: ^{a}from ^{1}H NMR; ^{b}from mass spectroscopy.
sat/uns=molar ratio diphenylpentanone/diphenylpentenone; nd=not determined.
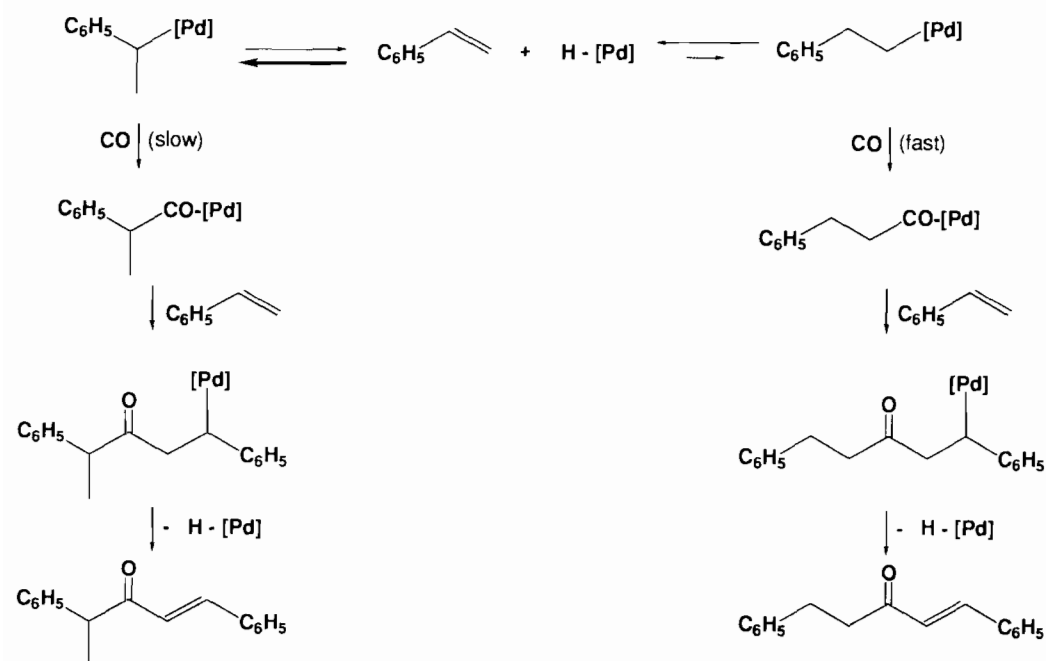
Scheme 2.

primary alkyl–metal species thus leads to the presence of deuterium in position 5 of the ketones and to the formation of products containing more than two deuterium atoms, respectively. It is to be noted that according to the above line of reasoning the high deuterium content at position 5 implies that prevailing secondary insertion of styrene in the palladium–hydride bond takes place. The labeling pattern obtained for the products from the carbonylation of styrene in the presence of dideuterium (the corresponding data are also

reported in Table 1) is in keeping with this interpretation.

A reversible insertion of styrene seems to take place also when a catalytic system formed *in situ* from [Pd(CH$_3$CN)$_4$][BF$_4$]$_2$ and Ph$_2$PCH$_2$CH$_2$SC$_2$H$_5$ (PSEt) is used for the carbonylation of styrene in the presence of dideuterium (Table 1). This latter system was previously found to cause largely regioselective (92%) formation of *E*-1,4-diphenylpent-1-en-3-one [3b]. The presence of deuterium at position 2 can, in fact, again be interpreted on the basis of reversible insertion of styrene into a palladium–deuteride bond followed by elimination and dissociation of the labeled olefin; this olefin will then participate in the formation of the ketone.

Particularly interesting is the label distribution in the saturated ketones. The low deuterium content of the product obtained from the carbonylation of styrene in the presence of dideuterium shows that this product does not arise (at least to a large extent) from hydrogenation of the previously formed unsaturated ketone. Hydrogenation of this compound is observed only at long reaction times. As possible mechanistic pathways either protonation of the intermediate palladium–alkyl species or binuclear elimination from the same species and a palladium–protide compound (arising from β-hydrogen elimination from a palladium alkyl intermediate, see also Scheme 2) should rather be considered. Protonation of palladium–alkyl intermediates has been proposed for the termination of the chain in the alternating copolymerisation of olefins with carbon monoxide [4i, 12]. Also the deuterium distribution of the unsaturated ketones in the reactions with dideuterium clearly indicates that the direct activation of dihydrogen by these catalysts is not easy at all, as the palladium–hydride species are evidently almost exclusively obtained by β-hydrogen elimination.

Dialkoxycarbonylation to succinate and hydroalkoxycarbonylation

Phosphine modified cationic palladium compounds are able to catalyse the hydrocarbomethoxylation of olefins [13]. When styrene is the substrate the presence of benzoquinone as the oxidant and certain diphosphine ligands was found to change the selectivity towards the formation of dimethyl phenylsuccinates [5, 8]. The dicarbonylation of *E*-β-deuteriostyrene (isotopic purity 91%) to dimethyl 2-phenylbutanedioate with [Pd(CF$_3$-COO)$_2$(Diop)] in the presence of Sn(CF$_3$SO$_3$)$_2$ was found to imply a clean *syn*-addition and complete retention of the label [8]. No information on label distribution in the monoester coproducts (methyl-2-phenylpropanoate and methyl-3-phenylpropanoate) was obtained.

In order to gain some information on the nature of the possible intermediates responsible for the formation of mono- an diesters [14] we have carried out the carbonylation of α-deuteriostyrene (isotopic purity >99%) using methanol and of styrene using CH$_3$OD with the above catalytic system both in the presence and in the absence of 1,4-benzoquinone. The results are summarized in Table 2 (see also Chart 1). Dimethyl 2-phenylbutanedioate and methyl cinnamate are formed only in the presence of the oxidant 1,4-benzoquinone; the regioselectivity in the formation of the monoesters under both sets of conditions is ∼1/1.

Within the limits of detection the reactions with α-deuteriostyrene gave only ester products containing one deuterium atom, both under oxidative and non-oxidative reaction conditions. For the reactions with unlabeled styrene the situation was somewhat different. Under non-oxidative reaction conditions small amounts of non-deuterated esters were obtained. Relatively large amounts of non-deuterated ester, as well as small amounts of dideuterated ester, were obtained under oxidative reaction conditions. The presence of dideuterated products could not be determined quantitatively from the GC-MS data, but was evident from the ^{13}C NMR spectra.

The fact that of the two possible regioisomeric unsaturated esters only methyl cinnamate is formed suggests that the same palladium–carbomethoxy species could be responsible for the formation of this compound and of dimethyl phenylsuccinate. In the formation of methyl cinnamate by palladium–protium elimination from a β-(alkoxycarbonyl)alkyl palladium species, palladium–protide species are generated. These account for some of the methyl phenylpropionates containing no deuterium for experiment 4 but not for all (as calculated from the amount of methyl cinnamate formed). Moreover, also in experiment 2, in which no methyl cinnamate is produced, non-deuterated esters are formed to some extent. Therefore, it seems that palladium–hydride species are formed via another reaction pathway as well. Oxidation of methanol to formaldehyde could lead to the formation of palladium hydrides [15].

The formation of the two esters in which intramolecular scrambling of the deuterium atom has taken place (**C** and **D** in Chart 1) can only be explained by assuming that at least part of the reaction runs via a palladium–hydride cycle. The larger extent of deuterium scrambling with unlabeled styrene than with α-deuteriostyrene might arise from reversible addition of a palladium–hydride and the existence of a positive deuterium-isotope effect for β-hydrogen elimination from palladium–alkyl intermediates. It is known that in the elimination of olefins from deuterated complexes of platinum and rhodium such a primary isotope effect

TABLE 2. Inter- and intramolecular deuterium distribution for the products arising from hydrocarbomethoxylation and biscarbomethoxylation of styrene using labeled substrates

Exp.	Substrates	Methyl ester considered and selectivity (%)	Intramolecular deuterium distribution[a]				Intramolecular deuterium distribution[b] A/D or B/C
			d_0	d_1	d_2	MDN	
1	$C_6H_5CD=CH_2$ $+CH_3OH$	2-phenylpropanoate, 30	~0	~100	~0	1.00	
		3-phenylpropanoate, 30	~0	~100	~0	1.00	
2	$C_6H_5CH=CH_2$ $+CH_3OD$	2-phenylpropanoate, 45	7	93	~0	0.93	96/4
		3-phenylpropanoate, 45	4	96	~0	0.96	92/8
3	$C_6H_5CD=CH_2$ $+CH_3OH$ $(+1,4-BQ)$	2-phenylpropanoate, 10.6	~0	~100	~0	1.00	
		3-phenylpropanoate, 10.9	~0	~100	~0	1.00	
		cinnamate, 4.8	n.d.	n.d.	n.d.	n.d.	
		2-phenylsuccinate, 42.7	1	99	~0	0.99	
4	$C_6H_5CH=CH_2$ $+CH_3OD$ $(+1,4-BQ)$	2-phenylpropanoate, 15.9	25	75	~0	~0	90/10
		3-phenylpropanoate, 16.4	23	77	~0	~0	90/10
		cinnamate, 5.7	n.d.	n.d.	n.d.	n.d.	
		2-phenylsuccinate, 27.5	94	6	~0	~0.06	

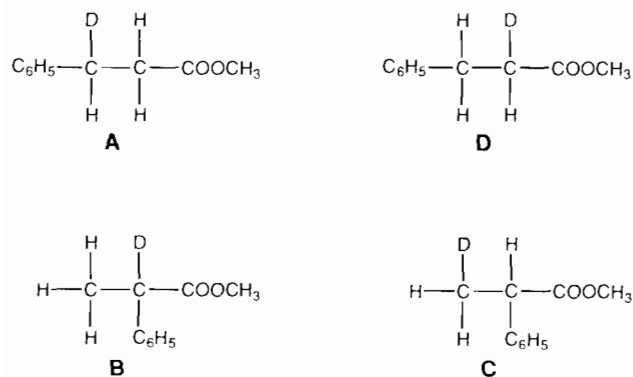[a]From MS data; for the monoester from GC-MS. [b]From ^2H NMR (see Chart 1).

Chart 1.

may exist [16]. Based on the results of the reactions with α-deuteriostyrene and deuteriomethanol, it seems probable that the formation of saturated monoesters takes place via a palladium–hydride cycle both under oxidative and under non-oxidative reaction conditions.

Conclusions

The copolymerisation of styrene with carbon monoxide using palladium cationic systems modified with dinitrogen ligands in the presence of 1,4-benzoquinone in methanol shows the typical *syn*-stereochemistry expected for a coordination polymerisation [17]. The polyketone chain can grow on either a palladium–carbomethoxy species or, when the oxidant is absent, on a palladium–hydride species. Under the latter conditions, however, a higher temperature is necessary for the growth of the chain. The reasons why in te-

trahydrofuran as the solvent in the presence of dihydrogen only the linear ketones and no polymeric material is produced are at the moment not fully understood. Also not clear are the factors that cause a different prevailing regioselectivity of the insertion of the first styrene unit in the formation of the ketones and of poly(1-oxo-2-phenyltrimethylene) in methanol as the solvent and in the presence of traces of hydrogen.

Diphosphine ligands seem to cause a more rapid β-hydrogen elimination reaction thus leading to the formation of *E*-1,5-diphenylpent-1-en-3-one. Owing to rapid β-hydrogen elimination after the first olefin insertion the regioselectivity of the reaction is due to a much slower rate of carbon monoxide insertion for the branched than for the linear metal–alkyl intermediate, as least when $[Pd(p-CH_3C_6H_4SO_3)_2(Dppp)]\cdot2H_2O$ is used as the catalyst precursor. The presence of 1,4-benzoquinone brings about again the formation of a palladium–carbomethoxy species that can evolve after consecutive styrene and carbon monoxide insertions to the succinate by alcoholysis. The methyl propionates could be either formed starting with a palladium–carbalkoxy or with a palladium–hydride species. Based on the label scrambling observed in the reactions using α-deuteriostyrene and deuteriomethanol the presence of palladium–hydride species even under oxidative reaction conditions appears, however, probable. Therefore, we cannot exclude that under both sets of conditions the formation of saturated monoesters takes place through a palladium–hydride cycle. Finally it is worth mentioning that apparently in palladium–carbalkoxy species as in palladium–acyl species secondary insertion of styrene takes place preferentially.

Experimental

Starting materials

$Sn(CF_3SO_3)_2$, 2,2'-bipyridine and hydroquinone were purchased from Fluka. 1,4-Benzoquinone and $Pd(CF_3COO)_2$ were purchased from Aldrich. Methanol was dried according to normal procedures and distilled under nitrogen. $[Pd(CF_3COO)_2(R,R\text{-diop})]$ was synthesised following literature procedures for analogous compounds. trans-β-Deuteriostyrene (isotopic composition $d_0 = 9\%$, $d_1 = 91\%$) was prepared according to the literature procedure [18]. α-Deuteriostyrene (isotopic composition $d_1 > 99\%$) was a Merck, Sharp & Dohme product.

General procedures

The NMR spectra were measured on a Bruker AM 300 WB or a Bruker AC 200 spectrometer with tetramethylsilane as the internal standard. Gas chromatographic analyses were carried out on a Shimadzu 8A GC with flame ionisation detector using a 10 m (0.20 mm i.d.) cross-linked methyl silicone capillary column or a Hewlett Packard 5890 II GC with flame ionisation detector using a 25 m (0.32 mm i.d.) cross-linked methyl silicone capillary column. Helium was used as the carrier gas.

Synthesis of $[Pd(p\text{-}CH_3C_6H_4SO_3)_2(Dppp)]\cdot 2H_2O$

0.200 g of $[PdCl_2(Dppp)]$ (0.339 mmol) was suspended with 0.192 g (0.688 mmol) of $Ag(p\text{-}CH_3C_6H_4SO_3)$ in 30 ml acetone and 10 ml methanol. A white precipitate was formed after a few minutes. The precipitate was filtered off on celite and the volume of the solution was reduced to 1/3. Addition of diethyl ether caused precipitation of yellow needles, which were filtered and dried. Yield. 0.258 g (0.287 mmol), 85%.

Anal. Calc. for $C_{41}H_{40}O_6P_2S_2Pd\cdot 2H_2O$ (MW 896.36): C, 54.88; H, 4.91; P, 6.92; S, 7.14. Found: C, 54.70; H, 4.83; P, 6.98; S, 7.27%. ^{1}H NMR (CDCl$_3$): 7.66 (m, 8H); 7.40 (m, 4H); 7.38 (d, 4H, $J = 8.1$); 7.25 (m, 8H); 6.86 (d, 4H, $J = 8.1$); 5.30 (b, 4H, H_2O); 2.79 (m, 4H); 2.30 (s, 6H); 2.21 (m, 2H). ^{31}P NMR (CDCl$_3$): 16.0. ^{13}C NMR (CDCl$_3$): 141.87 (s), 140.23 (s), 133.80 (t, $J^2_{CP} + J^4_{CP} = 5.5$ Hz), 132.30 (s), 129.25 (t, $J^3_{CP} + J^5_{CP} = 5.8$ Hz), 128.74 (s), 126.33 (s), 125.10 (m), 22.61 (t, $J^1_{CP} + J^3_{CP} = 22.3$ Hz), 21.37 (s), 18.70 (s).

Hydro-methoxycarbonylation of α-deuteriostyrene

In a nitrogen-filled glovebox a glass insert was charged with 28.7 mg (0.0345 mmol) $[Pd(CF_3COO)_2(R,R\text{-diop})]$, 14.4 mg (0.0345 mmol) $Sn(CF_3SO_3)_2$, 3.7 g (14 mmol) benzoquinone, 4 ml methanol and 0.9 g (0.87 mmol) α-deuteriostyrene. The glass insert was put in a 250 ml stainless steel autoclave. The autoclave was closed, flushed with CO once and pressurised to the 360 bar

CO pressure. The autoclave was placed in an oilbath and mechanically shaken. The reaction was monitored by the decrease in CO pressure. After 72 h at 30 °C the reaction was stopped. The autoclave was cooled to room temperature, the gas was vented and the reaction mixture removed from the autoclave for analysis and workup. A conversion of 75% was obtained. Product distribution: 42.9% methyl-2-phenylpropionate, 46.6% methyl-3-phenylpropionate and 10.5% other products.

The products were isolated by Kugelrohr distillation followed by column chromatography on silica, using chloroform as the solvent.

Methyl 2-deuterio-2-phenylpropionate. ^{1}H NMR (CDCl$_3$): 1.49 (s, 3H, CH$_3$); 3.67 (s, 3H, OCH$_3$); 7.0–7.4 (m, 5H, C$_6$H$_5$). ^{2}H NMR (CCl$_4$): 3.7. ^{13}C NMR (CDCl$_3$): 18.55 (s, CH$_3$); 45.11 (t, CD(C$_6$H$_5$), $J_{D-C} = 20$ Hz); 51.67 (s, OCH$_3$); 126–129 and 140.6 (6C, C$_6$H$_5$); 173.4 (CO$_2$CH$_3$). Isotopic composition: $d_0 = 0.2\%$, $d_1 = 99.8\%$ (based on the fragment at m/e 165).

Methyl 3-deuterio-3-phenylpropionate. ^{1}H NMR (CDCl$_3$): 2.62 (d, 2H, CH$_2$); 2.94 (m, 1H, CHD); 3.66 (s, 3H, OCH$_3$); 7.0–7.4 (m, 5H, C$_6$H$_5$). ^{2}H NMR (CCl$_4$): 2.9. ^{13}C NMR: 30.68 (t, CHD, $J_{D-C} = 20$ Hz); 35.7 (s, CH$_2$); 52.1 (s, OCH$_3$); 126–129 and 130.4 (6 C, C$_6$H$_5$); 175.1 (CO$_2$CH$_3$). Isotopic composition: $d_0 = 0.3\%$, $d_1 = 99.7\%$ (based on the fragment m/e 165).

Deuterio-methoxycarbonylation of styrene

Reaction procedures as above, starting with 0.906 g α-deuteriostyrene, 28.7 mg $[Pd(CF_3COO)_2(R,R\text{-diop})]$, 14.4 mg $Sn(O_3SCF_3)_2$ and 4 ml methanol. After 72 h at 30 °C (360 bar CO) a conversion of 56% was obtained. Product distribution: 35.9% methyl 2-phenylpropionate, 36.3% methyl 3-phenylpropionate and 27.8% other products.

Methyl 3-deuterio-2-phenylpropionate. ^{1}H NMR (CDCl$_3$): 1.49 (m, 2H, CH$_2$D); 3.71 (t, br, 1H, CH(C$_6$H$_5$)); 3.64 (s, 3H, OCH$_3$); 7.1–7.5 (m, 5H, C$_6$H$_5$). ^{2}H NMR: 1.5. ^{13}C NMR: 18.3 (t, CH$_2$D, $J_{D-C} = 20$ Hz); 45.3 (s, CH(C$_6$H$_5$)); 52.0 (s, OCH$_3$); 175.0 (s, CO$_2$CH$_3$). Isotopic composition: $d_0 = 6.7\%$, $d_1 = 93.3\%$ (based on the fragment m/e 165).

Methyl 2-deuterio-3-phenylpropionate. Due to overlap with the signals from other monoester products, no exact ^{1}H NMR or ^{13}C NMR data can be reported. ^{2}H NMR (CCl$_4$): 2.9. Isotopic composition: $d_0 = 3.8\%$, $d_1 = 96.2\%$ (based on the fragment m/e 165).

Hydro-methoxycarbonylation and bis-methoxycarbonylation of α-deuteriostyrene

Normal procedure as above. The glass insert was charged with 59 mg (0.071 mmol) $[Pd(CF_3COO)_2(R,R\text{-diop})]$, 29.6 mg (0.071 mmol) $Sn(O_3SCF_3)_2$, 1.86 g (17.2 mmol) benzoquinone, 7.5 ml methanol and 1.81 g (17.2 mmol) α-deuteriostyrene. Reaction time: 84 h at room

temperature. Conversion: 69.5%. Product distribution: 10.6% methyl 2-deuterio-2-phenylpropionate, 4.8% methyl 3-deuteriocinnamate, 10.9% methyl 3-deuterio-3-phenylpropionate, 42.7% dimethyl 2-deuterio-2-phenylsuccinate and 31% other (oligo- and polymeric) products. No deuterium was found incorporated in the hydroquinone.

Isotopic composition of methyl phenylpropionates (based on the fragment at m/e 165): methyl 2-deuterio-2-phenylpropionate: $\sim 100\%$ d_1; methyl 3-deuterio-3-phenylpropionate: $\sim 100\%$ d_1.

Methyl 3-deuteriocinnamate. ^{1}H NMR (CDCl$_3$): 3.81 (s, 3H, OCH$_3$); 6.44 (m, 1H, CH(CO$_2$CH$_3$)=CD(C$_6$H$_5$)); 7.0–7.4 (m, 5H, C$_6$H$_5$). ^{2}H NMR: 2.9. ^{13}C NMR: 51.76 (s, OCH$_3$), 144.6 (t, CD(C$_6$H$_5$), J_{D-C}=24 Hz); 117.8 (CH(CO$_2$CH$_3$)=CD(C$_6$H$_5$)); 126–129 and 134.4 (C$_6$H$_5$); 167.5 (CO$_2$CH$_3$).

Dimethyl 2-deuterio-2-phenylsuccinate. ^{1}H NMR (CDCl$_3$): 2.66 (d, 1H, CH$_2$, J_{H-H}=17.0 Hz); 3.21 (d, 1H, CH$_2$, J_{H-H}=17.0 Hz); 3.669 (s, 3H, OCH$_3$); 3.673 (s, 3H, OCH$_3$); 7.2–7.4 (m, 5H, C$_6$H$_5$. ^{2}H NMR (CDCl$_3$): 4.06. ^{13}C NMR (CDCl$_3$): 37.6 (s, CH$_2$); 46.8 (t, CD(C$_6$H$_5$); J_{D-C}=20 Hz); 51.92 (s, OCH$_3$); 52.39 (s, OCH$_3$); 127.8, 128.9 and 137.7 (6C, C$_6$H$_5$); 172.0 (CO$_2$CH$_3$); 173.5 (CO$_2$CH$_3$). Isotopic composition: d_0=1.3%, d_1=98.7% (based on the fragment at m/e 223.1).

Deuterio-methoxycarbonylation and bis-methoxycarbonylation of styrene

As described above starting with 87 mg (0.105 mmol) [Pd(CF$_3$COO)$_2$(R,R-diop)], 44 mg (0.105 mmol) Sn(O$_3$SCF$_3$)$_2$, 2.82 g (26.1 mmol) benzoquinone, 10 ml CH$_3$OD and 2.72 g (26.1 mmol) styrene. Reaction time: 84 h. Conversion: 69%. Product distribution: 15.9% methyl 2-deuterio-2-phenylpropionate, 5.7% methyl 3-deuteriocinnamate, 16.4% methyl 3-deuterio-3-phenylpropionate, 27.5% dimethyl 2-deuterio-2-phenylsuccinate and 34.5% other (oligo- and polymeric) products.

Isotopic composition of methyl phenylpropionates: methyl 2-phenylpropionates: d_0=25%, d_1=75% (based on the fragment at m/e 165); methyl 3-phenylpropionates: d_0=23%, d_1=77% (based on the fragment at m/e 165).

Isotopic composition of dimethyl phenylsuccinate d_0=93.7%, d_1=6.3% (based on the fragment at m/e 222.1).

Carbonylation of styrene to ketones

The carbonylation reaction of E-β-deuteriostyrene is described as an example. A solution of 1.3 ml E-β-deuteriostyrene in 10 ml of THF was introduced into a 150 ml stainless-steel autoclave containing 62.7 mg (0.07 mmol) of [Pd(p-CH$_3$C$_6$H$_4$SO$_3$)$_2$(Dppp)]·2H$_2$O. The autoclave was pressurised with 1 bar of H$_2$ and

20 bar of CO and heated up in an oil-bath at 100 °C for 20 h. After cooling and releasing of the gases, the mixture was analysed by capillary gas chromatography. The conversion of styrene was 98% with a yield in carbonylation products of 85%. The composition of the products was: 3-phenylpropanal (traces), 1,5-diphenylpentan-3-one (46%), E-1,5-diphenylpent-1-en-3-one (52%), other ketones (2%). The products (1,5-diphenylpentan-3-one and E-1,5-diphenylpent-1-en-3-one) were isolated by Kugelrohr distillation followed by column chromatography on silica, using hexane and methylene chloride as the solvent.

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