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Olefin insertion in Pd-acyl complexes modified with 1,4-C_s-symmetrical diphosphine ligands

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Abstract

The insertion of ethene and propene was investigated in palladium(II) acyl complexes of the type [PdC(O)CH_3(P^P′)(CH_3CN)](OTf) modified with the C_s-symmetric diphosphines **2**–**4** and the parent ligand **1**, described by C_{2v}-symmetry and taken as a reference.

Ethene insertion was investigated for acyl complexes containing the ligands **2** and **3**. Two insertion products formed in a ratio of approximately 1:1 for both systems, irrespective of the electronic properties of the ligands.

Propene as an α-olefin can insert according to a 1,2- or 2,1-insertion mode into a palladium acyl bond, arising regioselectivity issues. Moreover, due to the C_s-symmetry of the ligands, two stereoisomers can result upon insertion, as the alkyl group of the formed five-membered metallacycle can be *cis* or *trans* to each non-equivalent moiety. Propene insertion was indeed neither stereo- nor regioselective in the cases of **3** and **4**, in which the products arising from both 1,2- and 2,1-insertion were observed. **2** displayed total control of stereo- and regioselectivity, with the formation of one primary insertion product. Similar regioselectivity was observed for the reference ligand **1**. The regioisomeric distribution was different from equimolar for propene insertion, where the ratio of the products might be controlled by a combination of steric and electronic factors.

Keywords: Ethene insertion; Propene insertion; 1,4-C_s-symmetrical diphosphines; Pd-acyl complexes; Regioisomeric distribution

1. Introduction

Olefin insertion into acyl palladium complexes is a fundamental step of the copolymerization of olefins and carbon monoxide [1–3]. The reaction has been investigated independently [4–24] and in relation to the CO migratory insertion [25–41]. Few reports have been published dealing with propene insertion in acyl complexes modified with non-symmetrical ligands [21,42], in particular with relation to the catalysis.

Nozaki et al. reported the investigation of stepwise carbon monoxide and propene insertion in a palladium model complex modified with the non-symmetrical phosphine phosphite (*R*,*S*)-BINAPHOS [42]. Labeled dodecene insertion in the acyl complex [$Pd^{13}C(O)CH_3$(*R*,*S*)-BINAPHOS(CD_3CN)]BAr_4 (Ar = 3,5-$(CF_3)_2C_6H_3$), which exists as a single stereoisomer with the acyl group *trans* to the phosphine moiety, produced a mixture of two diastereoisomers, in ratio 4:1 (where the major compound had the alkyl group trans to the phosphine). The study reported by Nozaki shows how non-symmetrical ligands bring about issues of stereoselectivity upon insertion reaction in model complexes. The stereo- and regiocontrol achieved by (*R*,*S*)-BINAPHOS in the CO-propene copolymerization was almost complete. Copolymerization experiments of CO and propene with diphosphine ligands containing non-equivalent ligating moieties showed a high degree of control as well, even in the presence of remarkable electronic difference between the two dentates [43]. This NMR study is an attempt to rationalize the high regio- and stereocontrol achieved in the copolymerization.

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2. Results

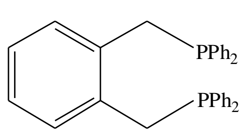
2.1. Olefin insertion in acyl complexes

Olefin insertion into an acyl complex results in an alkyl complex, in which the ketone oxygen coordinates to the metal to form a five-membered ring [22,25,26]. In this study, the acyl complexes [PdC(O)CH_3(P^P′)(CH_3CN)](OTf) (where P^P′ = **1**–**4**, Fig. 1) were generated *in situ* by bubbling CO or ^{13}CO through a metallic needle for 5–10 min into a $CDCl_3$ 0.04 M solution of the cationic complexes [PdCH_3(P^P′)(CH_3CN)](OTf) at −60 °C. 25–28 equivalents of the olefin (ethene, propene) were then added through a gastight syringe to the solution of the complex. At −60 °C no insertion of the olefin was observed even after several hours. Insertion occurred when the solution was warmed up to −20 °C. The NMR spectra for the characterization of the insertion products were recorded at this temperature. The low temperature was necessary to avoid the decomposition of the insertion product *via* β-H elimination [8].

From the point of view of regiochemistry the insertion of an α-olefin such as propene into a palladium acyl bond can occur either by primary (1,2) or secondary (2,1) mode. Additionally, the formed alkyl group can be located *trans* or *cis* to each moiety of the C_s-symmetric ligand, thus forming two products for each insertion mode (Fig. 2) [42]. The insertion modes of the olefin are competitive. However, in most of the cases one mode was preferred to the other. The identification of the isomers resulting from the prevailing insertion mode was achieved through multinuclear 1D and 2D NMR experiments. The isomers resulting from the less preferred insertion mode were generally present in small amount and their resonances were often overlapping those of the other pair of isomers. Their identification and partial characterization was possible only by employing labeled ^{13}CO.

2.2. Insertion of ethene in [PdC(O)CH_3(P^P′)(CH_3CN)](OTf) (P^P′ = **2**, **3**)

Ethene insertion was studied for the acyl complexes of the ligands **2** and **3**. Regiochemical issues are not involved.



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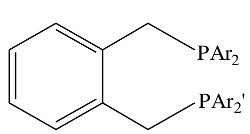

2: Ar = C_6H_5 Ar′ = 3-$CF_3C_6H_4$

3: Ar = 4-$CH_3OC_6H_4$ Ar′ = C_6H_5

4: Ar = 4-$CH_3OC_6H_4$ Ar′ = 3-$CF_3C_6H_4$

2-4

Fig. 1. Diphosphine ligands used.

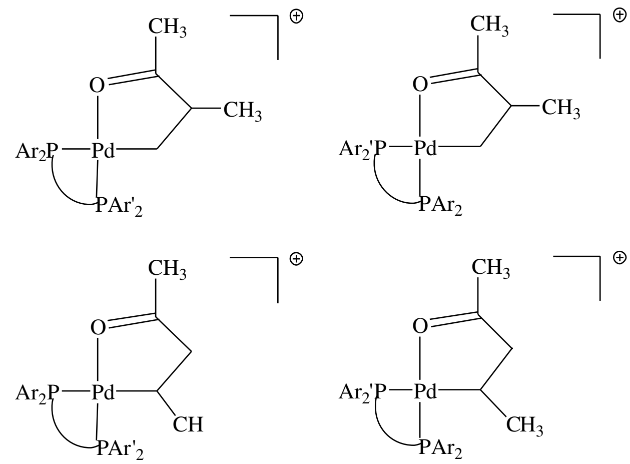

Fig. 2. Possible products resulting from the primary and secondary insertion of propene into the acyl complex [PdC(O)CH_3(P^P′)(CH_3CN)](OTf). P^P′: C_s-symmetrical diphosphine (Ar ≠ Ar′, **2**–**4**).

Insertion of ethene in the species [PdC(O)CH_3(**2**)(CH_3CN)](OTf), which exists as a mixture of two isomers in a ratio 2.6:1 [44], led to a mixture of two stereoisomers in ratio *ca.* 1:1 (ratio of the acyl group signals in the ^{1}H NMR spectrum). The ^{31}P{^{1}H} NMR spectrum showed two pairs of doublets. The signals of the methylene group PdCH_2 (H_α) appeared quite broadened and were observed at 1.64–1.65 ppm, while the methylene group in the β position with respect to the metal, CH_2C(O) (H_β), gave a broad singlet in the region 3.00–3.20 ppm. β-H elimination seemed to be less relevant than in the case of the alkyl complexes resulting from the propene insertion (see below). The ratio of the stereoisomers was changed to approximately equimolar when compared to the acyl precursors. The most relevant NMR data are reported in Tables 1 and 2.

Ethene insertion was also studied for the system [PdC(O)CH_3(**3**)(CH_3CN)](OTf). The complex was generated *in situ* by bubbling CO in a $CDCl_3$ solution of the palladium methyl complex for *ca.* 5 min at −60 °C. The acyl complex was formed as a mixture of isomers in ratio 1.8:1 [44]. In the major isomer M the acyl group occupies the position *trans* to the PPh_2 moiety, according to the *trans* influence concept. Upon insertion of ethene the five-membered ring, in which the ketone oxygen coordinates to the metal, was formed. Two products were formed after the ethene insertion in a ratio 1:1. Also in this case the ^{31}P{^{1}H} NMR spectrum showed two pairs of doublets. The phosphorus signals resulted both shifted downfield with respect to those measured for the acyl complex. The shift observed for the P_{cis} to the alkyl group was in the order of 14 ppm and was bigger than that observed for the P_{trans} (2–4 ppm). The peaks of the ring protons appeared quite broad but distinctly at 253 K. The protons of the PdCH_2 group (H_α) were found in the range 1.20–1.55 ppm, while those of the $CH_2C(O)CH_3$ (H_β) were shifted downfield between *ca.* 3.10 and 3.50 ppm.

In the region between 4.00 and 4.50 ppm the ^{1}H–^{31}P{^{1}H} correlation spectrum showed the cross peaks

Table 1
Relevant ^{1}H NMR data (δ ppm, $CDCl_3$; $T = 298$ K) for the ethene insertion products of [PdC(O)CH_3(**2**)(CH_3CN)](OTf)

Ethene insertion	PdCH_α δ (ppm)	PdCH_α δ (ppm)	CH_βC(O) δ (ppm)	CH_βC(O) δ (ppm)	C(O)CH_3 δ (ppm)	Ratio[a] M′:m′
M′, Pd–CH_2 bond *trans* to P(3-$CF_3C_6H_4$)$_2$	1.64	1.64	3.10	3.10	2.26	*ca.* 1:1
m′, Pd–CH_2 bond *trans* to PPh_2	1.65	1.65	3.20	3.20	2.28	*ca.* 1:1

[a] Ratio between the isomers calculated from the integration of the acyl groups in the ^{1}H NMR spectrum.

Table 2
Relevant ^{31}P{^{1}H} NMR data (δ ppm, $CDCl_3$; $T = 298$ K) for the ethene insertion products of [PdC(O)CH_3(**2**)(CH_3CN)](OTf)

Ethene insertion	P_{trans} δ (ppm)	P_{cis} δ (ppm)	$^2J_{P-P}$ (Hz)	Ratio[a] M′: m′
M′, Pd–CH_2 bond *trans* to P(3-$CF_3C_6H_4$)$_2$	4.5	34.7	40.7	*ca.* 1:1
m′, Pd–CH_2 bond *trans* to PPh_2	4.9	34.5	41.5	*ca.* 1:1

P_{cis} and P_{trans} describe the phosphorus atom *cis* and *trans* to the alkyl group, respectively.
[a] Ratio between the isomers calculated from the integration of the acyl groups in the ^{1}H NMR spectrum.

between the phosphorus atoms and the benzylic methylene groups of the ligand. The signals in the ^{1}H NMR spectrum were broad and overlapped, but the cross peaks were observed distinctly. Tables 3 and 4 summarize the relevant NMR data for the ethene insertion products of [PdC(O)-CH_3(**3**)(CH_3CN)](OTf).

2.3. Insertion of propene in [PdC(O)CH$_3$(3)(CH$_3$CN)](OTf)

Upon propene insertion in [PdC(O)CH_3(**3**)(CH_3CN)](OTf) four stereoisomers were formed, as one could immediately see from the number of the acyl peaks in the region 2.05–2.35 ppm. The four products formed in a ratio M^I:m^I:M^{II}:m^{II} = 7:4.7:1:1 (overall ratio normalized to m^{II}). The main products resulted from a preferred primary insertion of propene (M^I and m^I: major and minor isomers), while the minor products M^{II} and m^{II} originated from the secondary insertion. The assignment of the regiochemistry of the insertion was possible by combining the information afforded by ^{1}H–^{31}P correlation, ^{1}H-TOCSY and ^{1}H–^{13}C correlation and by comparison with the data obtained from the ethene insertion study into the acyl complex. In the ^{31}P{^{1}H} NMR (Fig. 3) one could recognize two pairs of doublets corresponding to the primary insertion products. Upon insertion of the olefin all the phosphorus resonances underwent a shift downfield (*i.e.*, from δ 0.9 and 17.5 ppm for P_{trans} and P_{cis}, respectively, in the major isomer of [PdC(O)CH_3(**3**)(CH_3CN)](OTf) to 3.3 and 32.3 for P_{trans} and P_{cis}, respectively, in M^I); the shift was bigger for the P_{cis} to the alkyl group than for the P_{trans}. Part of the acyl complex underwent decarbonylation, so that the alkyl palladium complex could be still observed in spectrum (indicated with D). The phosphorus resonances for the secondary insertion products were overlapped with those of the primary insertion products.

For the isomer M^I the P_{trans} to the alkyl group was found at 3.3 ppm and the P_{cis} at 32.3 ppm, while for the isomer m^I P_{trans} appeared at 0.9 ppm and P_{cis} at 34.9 ppm. The multiplicity of each phosphorus signal was a doublet due to the coupling with the non-equivalent moiety of the ligand. The $^2J_{P-P}$ for the isomer M^I was 43.0 Hz, while that for the isomer m^I was 42.2 Hz. The phosphorus signals for the secondary insertion products M^{II} and m^{II} are probably overlapped with those of M^I and m^I (see below).

Table 3
Relevant ^{1}H NMR data (δ ppm, $CDCl_3$; $T = 253$ K) for the ethene insertion products of [PdC(O)CH_3(**3**)(CH_3CN)](OTf)

Ethene insertion	PdCH_α δ (ppm)	PdCH_α δ (ppm)	CH_βC(O) δ (ppm)	CH_βC(O) δ (ppm)	C(O)CH_3 δ (ppm)	Ratio[a] M′:m′
M′, Pd–CH_2 bond *trans* to PPh_2	1.20	1.52	3.16	3.50	2.30	*ca.* 1:1
m′, Pd–CH_2 bond *trans* to P(4-$CH_3OC_6H_4$)$_2$	1.24	1.54	3.14	3.40	2.28	*ca.* 1:1

[a] Ratio between the isomers calculated from the integration of the acyl groups in the ^{1}H NMR spectrum.

Table 4
Relevant ^{31}P NMR data (δ ppm, $CDCl_3$; $T = 253$ K) for the ethene insertion products of [PdC(O)CH_3(**3**)(CH_3CN)](OTf)

Ethene insertion	P_{trans} δ (ppm)	P_{cis} δ (ppm)	$^2J_{P-P}$ (Hz)	Ratio[a] M′:m′
M′, Pd–CH_2 bond *trans* to PPh_2	0.9	34.6	41.5	*ca.* 1:1
m′, Pd–CH_2 bond *trans* to P(4-$CH_3OC_6H_4$)$_2$	3.2	32.0	43.0	*ca.* 1:1

P_{cis} and P_{trans} describe the phosphorus atom *cis* and *trans* to the alkyl group, respectively.
[a] Ratio between the isomers calculated from the integration of the acyl groups in the ^{1}H NMR spectrum.

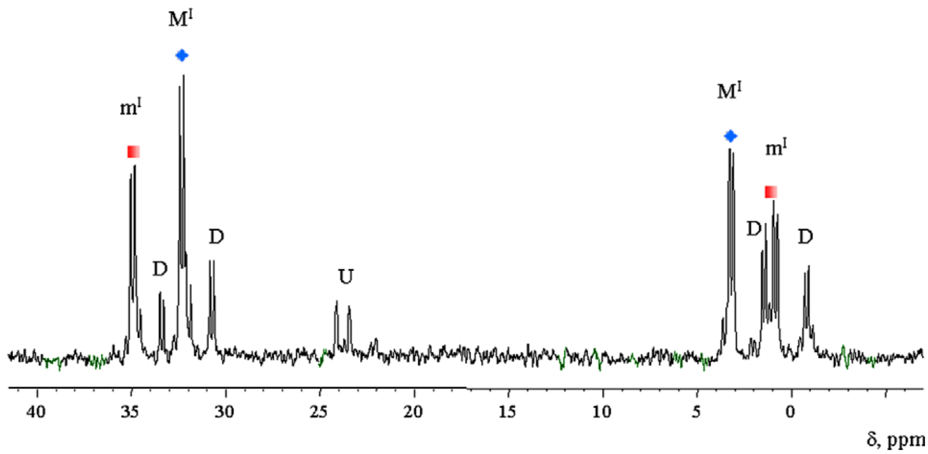

Fig. 3. Detail of the $^{31}P\{^{1}H\}$ NMR spectrum (δ ppm, $CDCl_3$; $T = 253$ K) for the propene insertion products of [$PdC(O)CH_3$(**3**)(CH_3CN)](OTf). The alkyl palladium complex, resulting from the decarbonylation of the *in situ* formed acyl complex [$PdC(O)CH_3$(**3**)(CH_3CN)](OTf), can be recognized (peaks indicated with D = decarbonylation products). U = unidentified products.

The main pair of stereoisomers was characterized by means of ^{1}H–^{31}P correlation spectroscopy. Three cross peaks at about δ 1.30, 1.60 and 3.00 ppm are detected. The broad signals at *ca.* 1.30 and 1.60 ppm (the latter overlapped with the –CH_3 residual peak of the non-inserted propene) were assigned to methylene diastereotopic protons directly bound to the metal, CH_2Pd (H_α), while that at *ca.* 3.00 ppm described the methine group $CHCH_3$ (H_β). For the same insertion mode, e.g., 1,2-insertion, the protons of the two stereoisomers M^I and m^I appeared overlapped in the ^{1}H NMR spectrum. From the cross peaks in the ^{1}H–^{31}P correlation spectrum the major stereoisomer resulting from the primary insertion of propene into the acyl complex (M^I) was identified. In M^I the alkyl group occupied the position *trans* to PPh_2, as in the major isomer of the acyl complex [$PdC(O)CH_3$(**3**)(CH_3CN)](OTf). From the ^{1}H–^{31}P correlation spectrum the identification of the secondary insertion products M^{II} and m^{II} was not straightforward. On one hand the $^{31}P\{^{1}H\}$ NMR signals of M^{II} and m^{II} were overlapped to those of the primary insertion products, as M^{II} and m^{II} were present in small concentration in the system. On the other hand the chemical shifts of their alkyl protons were slightly different from those of M^I and m^I. ^{1}H-TOCSY correlation spectroscopy allowed the identification of the two diastereotopic protons $CH_2C(O)CH_3$ (H_β). One appeared as a multiplet at *ca.* 2.51 ppm, while the other overlapped with the signals of the methine groups of M^I and m^I at *ca.* 3.00 ppm. All the signals describing the alkyl groups of the five-membered ring appeared quite broadened. Methylene and methyne protons showed a cross peak with the methyl groups of the diastereoisomeric complexes, which were found as overlapped doublets in the region 1.04–1.16 ppm for the four species.

In a separate experiment the acyl complex was generated from [$PdCH_3$(**3**)(CH_3CN)](OTf) by bubbling ^{13}CO and was subsequently treated with propene according to the described procedure. This kind of experiment provided the most straightforward way to identify the two pairs of regioisomers. In the ^{1}H NMR (Fig. 4) the methyl of the acyl groups appeared now as doublets for the coupling of the protons with the ^{13}C of the labeled ^{13}CO. The $^{2}J_{H–C}$ ranged between 5.78 and 6.07 Hz.

The ^{1}H–^{13}C correlation displayed four different peaks in the carbonyl region (238–241 ppm), corresponding to the ketone groups of the formed stereoisomers. Each carbonyl group appeared as a doublet for the coupling with the phosphorus atom in position *trans* to the ketone group. The primary insertion products M^I and m^I gave two doublets at δ 238.4 and 238.6 ppm, respectively, while the secondary insertion products M^{II} and m^{II} were found at 240.0 and 240.2 ppm. The $^{3}J_{C–P}$ was in all the cases 8.0 Hz. The ^{1}H–^{13}C correlation (Fig. 5) showed the cross peak of the methyne group $PdCHCH_3$ (H_α) for M^{II} and m^{II} with the carbonyl carbon at *ca.* 1.15 ppm (almost overlapped with the methyl groups of the four isomers) and confirmed the assignments of the alkyl protons that had been already observed from the ^{1}H-TOCSY experiment.

Tables 5 and 6 summarize the most relevant NMR parameters for the primary and secondary insertion products of [$PdC(O)CH_3$(**3**)(CH_3CN)](OTf). Table 7 reports the important NMR parameters acquired through experiments with labeled ^{13}CO.

The same kind of study was carried out for the acyl complexes [$PdC(O)CH_3$(P^P′)(CH_3CN)](OTf) (where P^P′ = **1**, **2** and **4**). In the case of **1**, the parent C_{2v}-symmetrical ligand, the acyl complex [$PdC(O)CH_3$(**1**)(CH_3CN)](OTf) exists as a single isomer. The ^{1}H NMR spectrum showed the acyl group as a broad singlet at δ 2.22 ppm. From the ^{1}H-TOCSY experiment of the insertion product cross peaks at δ 1.34, 1.58 and 3.04 ppm were observed. From the comparison with the results obtained for **3**, the species formed corresponded to a primary insertion product of the olefin. No secondary insertion product was detected. The $^{31}P\{^{1}H\}$ NMR showed two doublets at δ 3.15 and at 35.2 ppm, corresponding to P_{trans}, and P_{cis} to

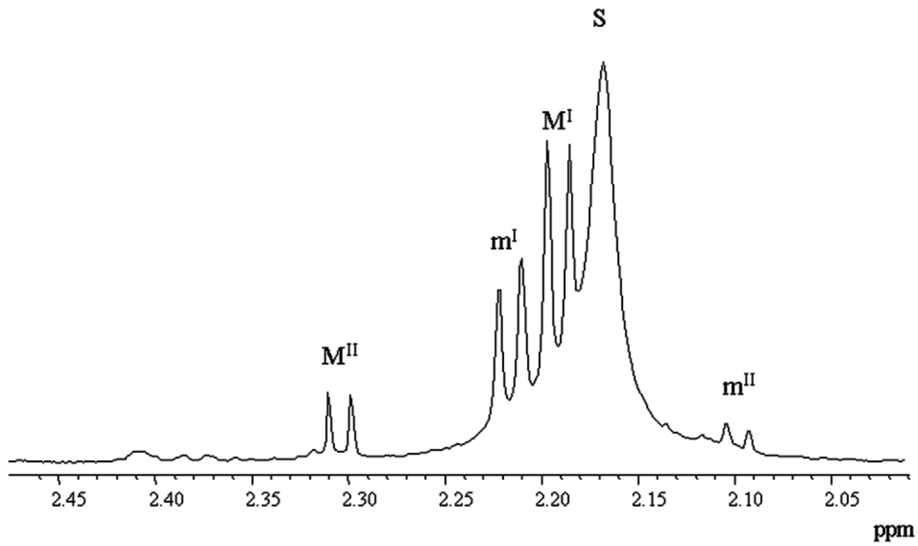

Fig. 4. Detail of the acyl groups region in the ^{1}H NMR spectrum (δ ppm, $CDCl_3$; $T = 253$ K) for the propene insertion products of $[Pd^{13}C(O)CH_3(\mathbf{3})(CH_3CN)](OTf)$ (M^{I}: major isomer for primary insertion, M^{II}: major isomer for secondary insertion). Free acetonitrile (indicated as S, solvent molecule) is observed as a broad peak at *ca.* 2.16 ppm. The ratio M^{I}:m^{I}:M^{II}:m^{II} was obtained by deconvolution of the acyl group peaks.

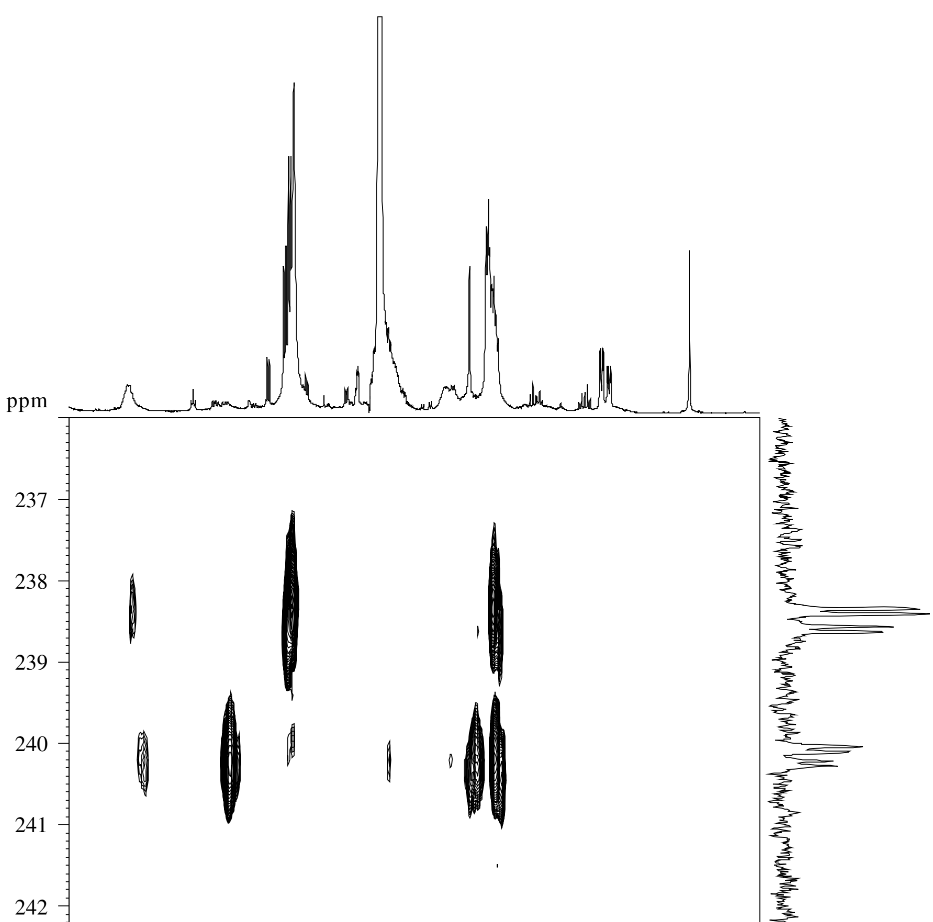

Fig. 5. Detail of the ^{1}H–^{13}C correlation experiment (δ ppm, $CDCl_3$; $T = 253$ K) of the propene insertion products of $[Pd^{13}C(O)CH_3(\mathbf{3})(CH_3CN)](OTf)$. The acyl carbonyl groups are visible as doublets in the ^{13}C NMR spectrum.

Table 5
Relevant ^{1}H NMR parameters (δ ppm, $CDCl_3$; $T = 253$ K) of the 1,2- and 2,1-propene insertion products of [PdC(O)CH_3(**3**)(CH_3CN)](OTf)

Primary insertion	$PdCH_\alpha$ δ (ppm)	$PdCH_\alpha$ δ (ppm)	$CH_\beta CH_3$ δ (ppm)	$CH_\beta CH_3$ δ (ppm)	C(O)CH_3 δ (ppm)	Ratio[a] M^I:m^I
M^I, Pd–CH_2 bond *trans* to PPh_2	1.64	1.36	3.04	1.09	2.19	1.5:1
m^I, Pd–CH_2 bond *trans* to P(4-$CH_3OC_6H_4$)$_2$	1.62	1.32	3.14	1.11	2.22	1.5:1
Secondary insertion	$PdCH_\alpha$ δ (ppm)	CH_β δ (ppm)	CH_β δ (ppm)	$CH_\alpha CH_3$ δ (ppm)	C(O)CH_3 δ (ppm)	Ratio[b] M^{II}: m^{II}
M^{II}	1.18	*ca.* 3	*ca.* 2.5	*ca.* 1.15	2.30	1:1
m^{II}	Overl.[c] *ca.* 1.20	Overl. *ca.* 3	Overl. *ca.* 2.5–2.6	Overl. *ca.* 1.15	2.10	1:1

The signals of the secondary insertion products were in some cases overlapped.
[a] Ratio M^I:m^I normalized to the concentration of m^I, calculated from deconvolution of the acyl groups in ^{1}H NMR.
[b] M^{II}:m^{II} normalized to the concentration of m^{II}, calculated from deconvolution of the acyl groups in ^{1}H NMR.
[c] Overlapping between M^{II} and m^{II}.

Table 6
Relevant $^{31}P\{^{1}H\}$ NMR parameters (δ ppm, $CDCl_3$; $T = 253$ K) of the 1,2- and 2,1-propene insertion products of [PdC(O)CH_3(**3**)(CH_3CN)](OTf)

Primary insertion	P_{trans} δ (ppm)	P_{cis} δ (ppm)	$^{2}J_{P-P}$ (Hz)	Ratio[a] M^I:m^I
M^I	3.0	32.3	43.0	1.5:1
m^I	0.6	34.9	42.2	1.5:1
Secondary insertion	P_{trans} δ (ppm)	P_{cis} δ (ppm)	$^{2}J_{P-P}$ (Hz)	Ratio[b] M^{II}:m^{II}
M^{II}	Overl.[c] *ca.* 1.0	Overl. *ca.* 32.0	n.o.[d]	1:1
m^{II}	Overl. *ca.* 3.0	Overl. *ca.* 35.0	n.o.	1:1

The signals of the secondary insertion products were in some cases overlapped. P_{cis} and P_{trans} describe the phosphorus atom *cis* and *trans* to the alkyl group, respectively.
[a] Ratio M^I:m^I normalized to the concentration of m^I, calculated from deconvolution of the acyl groups in ^{1}H NMR.
[b] M^{II}:m^{II} normalized to the concentration of m^{II}, calculated from deconvolution of the acyl groups in ^{1}H NMR.
[c] Overlapping between M^{II} and m^{II}.
[d] Not observed.

Table 7
Relevant ^{1}H and ^{13}C NMR data (δ ppm, $CDCl_3$; *T*: 253 K) for the acyl groups of the primary (M^I and m^I) and secondary (M^{II} and m^{II}) propene insertion products of [Pd^{13}C(O)CH_3(**3**)(CH_3CN)](OTf)

Primary insertion	^{1}H NMR ^{13}C(O)CH_3 δ (ppm)	$^{2}J_{H-C}$ (Hz)	^{13}C NMR ^{13} *C*(O)CH_3 δ (ppm)	$^{3}J_{C-P}$ (Hz)	Ratio[a] M^I:m^I	Overall ratio primary: secondary insertion[b]
M^I	2.19, d	6.07	238.4, d	8.0	1.5:1	5.9:1
m^I	2.22, d	6.07	238.6, d	8.0		
Secondary insertion	^{1}H NMR ^{13}C(O)CH_3 δ (ppm)	$^{2}J_{H-C}$ (Hz)	^{13}C NMR ^{13} *C*(O)CH_3 δ (ppm)	$^{3}J_{C-P}$ (Hz)	Ratio[c] M^{II}: m^{II}	
M^{II}	2.30, d	5.78	240.1, d	8.0	1:1	
m^{II}	2.10, d	6.07	240.2, d	8.0		

Multiplicity of the signals is reported.
[a] The ratio M^I:m^I is normalized with respect to the amount of m^I and calculated from the deconvolution of the acyl groups in the ^{1}H NMR spectrum.
[b] The overall ratio is normalized to the sum of the secondary insertion products $M^{II} + m^{II}$.
[c] The ratio M^{II}:m^{II} is normalized with respect to the amount of m^{II} and calculated from the deconvolution of the acyl groups in the ^{1}H NMR spectrum.

the alkyl group, respectively. The coupling constant $^{2}J_{P-P}$ was 41.5 Hz. Table 8 reports the relevant NMR data for this insertion study.

Propene insertion in [Pd^{13}C(O)CH_3(**4**)(CH_3CN)](OTf) showed the formation of primary and secondary insertion products. In the ^{1}H NMR spectrum three acyl groups, appearing as doublets for the coupling of protons with ^{13}C, were identified in the region 2.20–2.35 ppm (Fig. 6). From the ^{13}C spectrum one primary insertion product was identified (doublet at δ 239.2 ppm, $^{3}J_{C-P} = 9$ Hz, coupling with the P_{trans} to the alkyl group). The broad signal at δ *ca.* 240.9 ppm corresponded to the secondary insertion products (determined from ^{1}H–^{13}C correlation).

Deconvolution of the acyl peaks provided an estimation of the isomer distribution equal to M^I:M^{II}:m^{II} *ca.* 8.9:1.4:1. From the ^{1}H–^{31}P correlation spectrum the stereochemistry of the primary insertion product M^I was determined, corresponding to the alkyl group *trans* to P(3-$CF_3C_6H_4$)$_2$. No stereochemical information could be obtained for M^{II} and m^{II}, as there were no cross peaks for these species. The relevant ^{1}H and $^{31}P\{^{1}H\}$ NMR are reported in Tables 9 and 10.

Table 8
Relevant NMR data for the primary propene insertion product in $[PdC(O)CH_3(\mathbf{1})(CH_3CN)](OTf)$ (δ ppm, $CDCl_3$; $T = 253$ K)

Primary insertion					
^{1}H NMR	PdCH_α δ (ppm)	PdCH_α δ (ppm)	CH_βCH$_3$ δ (ppm)	CH$_\beta$CH_3 δ (ppm)	C(O)CH_3 δ (ppm)
	1.34	1.58	3.04	1.10	2.22
^{31}P{^{1}H} NMR	P_{trans} δ (ppm)	P_{cis} δ (ppm)	$^2J_{P-P}$ (Hz)		
	3.1	35.2	41.5		

P_{cis} and P_{trans} describe the phosphorus atom *cis* and *trans* to the alkyl group, respectively.

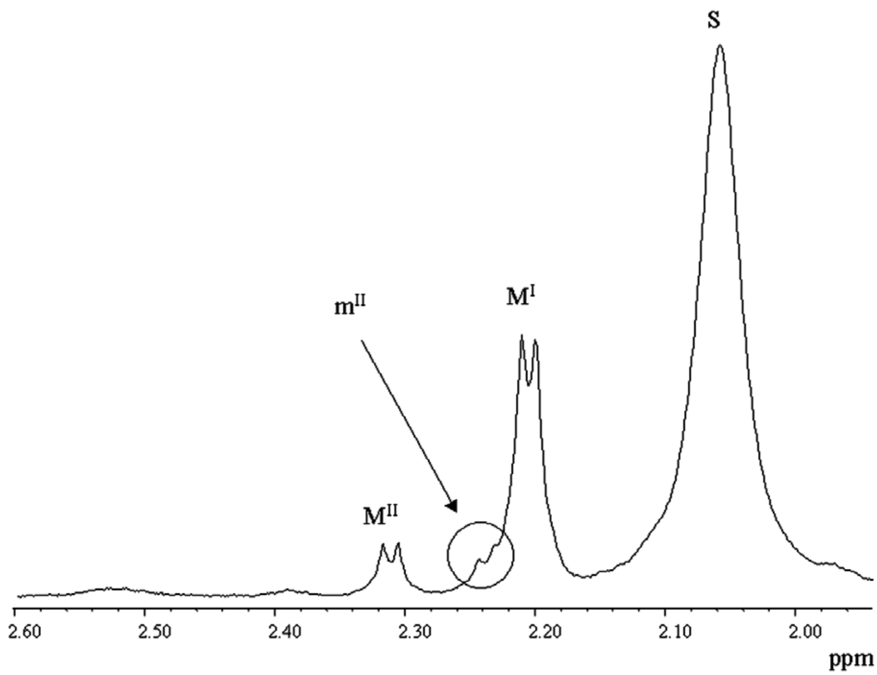

Fig. 6. Detail of the acyl groups region in the ^{1}H NMR spectrum (δ ppm, $CDCl_3$; $T = 253$ K) for the propene insertion products of $[Pd^{13}C(O)CH_3(\mathbf{4})(CH_3CN)](OTf)$ (M^I: major isomer for primary insertion, M^{II}: major isomer for secondary insertion). The acyl group for the species m^{II} appears as a shoulder at *ca.* 2.24 ppm. Free acetonitrile (indicated as S, solvent molecule) is observed as a broad peak at 2.06 ppm.

Table 9
Relevant ^{1}H NMR parameters (δ ppm, $CDCl_3$; $T = 253$ K) of the 1,2- and 2,1-propene insertion products of $[PdC(O)CH_3(\mathbf{4})(CH_3CN)](OTf)$

Primary insertion	PdCH_α δ (ppm)	PdCH_α δ (ppm)	CH_βCH$_3$ δ (ppm)	CH$_\beta$CH_3 δ (ppm)	C(O)CH_3 δ (ppm)	M^I
M^I, Pd–CH$_2$ bond *trans* to P(3-CF$_3$C$_6$H$_4$)$_2$	1.71	1.41	3.00–3.11	1.06–1.15	2.21	1 isomer primary insertion
Secondary insertion	PdCH_αCH$_3$ δ (ppm)	CH_β δ (ppm)	CH_β δ (ppm)	CH$_\alpha$CH_3 δ (ppm)	C(O)CH_3 δ (ppm)	Ratio[a] M^{II}:m^{II}
M^{II}	*ca.* 1.20–1.25	2.48–2.57	*ca.* 3.0	*ca.* 1.11	2.31	*ca.* 1.4:1
m^{II}	*ca.* 1.20–1.25	2.48–2.57	*ca.* 3.0	*ca.* 1.11	2.24	

The signals of the secondary insertion products were in some cases overlapped.
[a] The M^{II}:m^{II} was normalized to the concentration of m^{II}, calculated from deconvolution of the acyl groups in the ^{1}H NMR spectrum.

Propene insertion in $[PdC(O)CH_3(\mathbf{2})(CH_3CN)](OTf)$ afforded only one primary insertion product. The alkyl group occupied the position *trans* to the P(3-CF$_3$C$_6$H$_4$)$_2$, as in the case of the major isomer observed upon CO insertion into the palladium-alkyl group. The presence of the only primary insertion product was quite remarkable, as secondary insertion always took place in the case of the other C_s-symmetrical diphosphine ligands **3** and **4**. Assignments of the resonances were achieved by means of ^{1}H-TOCSY experiments. Tables 11–13 report the main NMR data for the obtained insertion product.

3. Discussion

The insertion of ethene and propene in palladium(II) acyl complexes modified with C_s-symmetrical diphosphine

Table 10
Relevant $^{31}P\{^1H\}$ NMR parameters (δ ppm, $CDCl_3$; $T = 253$ K) of the 1,2- and 2,1-propene insertion products of $[PdC(O)CH_3(\mathbf{4})(CH_3CN)](OTf)$

Primary insertion	P_{trans} δ (ppm)	P_{cis} δ (ppm)	$^2J_{P–P}$ (Hz)	M^I
M^I, Pd–CH_2 bond *trans* to $P(3\text{-}CF_3C_6H_4)_2$	4.4	32.4	41.5	1 isomer primary insertion
Secondary insertion	P_{trans} δ (ppm)	P_{cis} δ (ppm)	$^2J_{P–P}$(Hz)	Ratio[a] M^{II}:m^{II}
M^{II}	n.o.[b]	n.o.	n.o.	*ca.* 1.4:1
m^{II}	n.o.	n.o.	n.o.	

The signals of the secondary insertion products were too broad to be observed. P_{cis} and P_{trans} describe the phosphorus atom *cis* and *trans* to the alkyl group, respectively.
[a] The ratio M^{II}:m^{II} was normalized to the concentration of m^{II}, calculated from deconvolution of the acyl groups in the ^1H NMR spectrum.
[b] Not observed.

Table 11
Relevant ^1H NMR parameters (δ ppm, $CDCl_3$; $T = 253$ K) of the 1,2-propene insertion product of $[PdC(O)CH_3(\mathbf{2})(CH_3CN)](OTf)$

Primary insertion	$PdCH_\alpha$	$PdCH_\alpha$	$CH_\beta CH_3$	$CH_\beta CH_3$	$C(O)CH_3$	M^I
M^I, Pd–CH_2 bond *trans* to $P(3\text{-}CF_3C_6H_4)_2$	1.74	1.46	3.09	1.13	2.24	1 isomer observed

Table 12
Relevant $^{31}P\{^1H\}$ NMR parameters (δ ppm, $CDCl_3$; $T = 253$ K) of the 1,2-propene insertion product of $[PdC(O)CH_3(\mathbf{2})(CH_3CN)](OTf)$

Primary insertion	P_{trans} δ (ppm)	P_{cis} δ (ppm)	$^2J_{P–P}$ (Hz)	M^I
M^I, Pd–CH_2 bond *trans* to $P(3\text{-}CF_3C_6H_4)_2$	4.7	35.1	41.5	1 isomer primary insertion

P_{cis} and P_{trans} describe the phosphorus atom *cis* and *trans* to the alkyl group, respectively.

ligands did not display in general any selectivity, with the exception of **2** in the case of propene insertion. Upon ethene insertion the complexes containing **2** and **3** formed the two possible stereoisomers in ratio 1:1, in contrast to what observed with CO insertion into the corresponding palladium-methyl complexes. **2** and **3** are quite different under the electronic point of view. Having in common the PPh_2 moiety, **3** is more basic than **2**. One can conclude that the electronic nature of the ligand is not playing a relevant role for the stereoselectivity of the insertion, when the case of ethene is considered. Remarkably, the 1:1 ratio between the insertion products M and m differs from the initial stereoisomer distribution observed for the acetyl palladium complexes of **2** and **3**, which was 1.8:1 and 1.5:1, respectively [44]. This fact might indicate that the isomeric composition of the complexes reflects their relative thermodynamic stability. However, we have no reliable thermodynamic and kinetic data on this aspect. The *trans* influence of the methyl group in the palladium methyl complexes and that of the alkyl group in the ethene insertion products are similar. Therefore, other factors, such as the coordination of the ketone oxygen to the metal center, should play a role in the stabilization of these species.

In addition to the stereochemical control, regiochemical control must be taken into account in the case of propene insertion. Primary and secondary insertions were competitive, although the primary mode was prevailing in all the cases investigated. The ligand **1**, the only C_{2v}-symmetrical term of the series, inserted propene only according to a primary mode. Among the C_s-symmetrical terms, only $[PdC(O)CH_3(\mathbf{2})(CH_3CN)](OTf)$ gave exclusively primary insertion. **3** formed the four possible products upon insertion. **4** afforded one primary insertion product, as well as the two products derived from secondary insertion. The relative ratio primary:secondary insertion for each acyl complex was obtained by deconvolution of the peaks of the acyl groups in the ^1H NMR spectrum. For **3** the overall ratio between primary and secondary insertion products was 5.9:1, while for **4** was 3.7:1. **2** and **1** afforded efficient regiocontrol as no 2,1-insertion products were observed. Among the systems investigated, primary and secondary insertion were more competitive in $[PdC(O)CH_3(\mathbf{4})$-$(CH_3CN)](OTf)$.

The stereochemical control for the propene insertion in this kind of systems is reflected in the formation of one or two isomers for each insertion mode. Each regioisomer existed as a mixture of two different stereoisomers, where the alkyl group was *trans* to each non-equivalent phosphorus moiety. **3** afforded two stereoisomers for each insertion mode. The relative ratio M^I:m^I was 1.5:1, while the relative ratio M^{II}:m^{II} was 1:1. For **4** one stereoisomer was identified upon primary insertion, but the secondary insertion afforded the two isomers M^{II} and m^{II} (M^{II}:m^{II} *ca.* 1.4:1). Regarding the stereocontrol, **2** was the most efficient system of the series, as only one product was found upon primary insertion of propene. The C_{2v}-symmetry of **1** did not give rise to any stereocontrol issue. Apart from the total stereoselectivity of **2**, the stereocontrol achieved for each insertion mode was more efficient in **3**, with one prevailing product for each insertion mode. The results obtained can be summarized as follows.

Table 13
^{1}H and ^{13}C NMR data (δ ppm, $CDCl_3$; *T*: 253 K) for the acyl groups of the primary (M^I and m^I) and secondary (M^{II} and m^{II}) propene insertion products of $[Pd^{13}C(O)CH_3(P\hat{}P')(CH_3CN)](OTf)$ ($P\hat{}P'$ = **2**, **4**)

PP2	^{1}H NMR ^{13}C(O)CH_3 δ (ppm)	$^2J_{H-C}$ (Hz)	^{13}C NMR ^{13}C(O)CH$_3$ δ (ppm)	$^3J_{C-P}$ (Hz)	Ratio M^I:m^I	Overall ratio primary: secondary insertion
Primary insertion						
M^I	2.24, d	5.20	239.6, broad	n.o.[a]	Only M^I observed	Only M^I observed
PP4	^{1}H NMR ^{13}C(O)CH_3 δ (ppm)	$^2J_{H-C}$ (Hz)	^{13}C NMR ^{13}C(O)CH$_3$ δ (ppm)	$^3J_{C-P}$ (Hz)	Ratio M^I:m^I	Overall ratio primary: secondary insertion[b]
Primary insertion						
M^I	2.21, d	5.20	239.2, d	9.0	Only M^I observed	3.7:1
	^{1}H NMR ^{13}C(O)CH_3 δ (ppm)	$^2J_{H-C}$ (Hz)	^{13}C NMR ^{13}C(O)CH$_3$ δ (ppm)	$^3J_{C-P}$ (Hz)	Ratio[c] M^{II}:m^{II}	
Secondary insertion						
M^{II}	2.31	5.78	240.9, broad	n.o.	*ca.* 1.4:1	
m^{II}	2.24	6.35	240.9, broad	n.o.	*ca.* 1.4:1	

Multiplicity of the signals is reported.
[a] Not observed.
[b] The overall ratio is normalized to the sum of the secondary insertion products $M^{II} + m^{II}$ and calculated from the deconvolution of the acyl groups in the ^{1}H NMR spectrum.
[c] The ratio M^{II}:m^{II} is normalized with respect to the amount of m^{II} and calculated from the deconvolution of the acyl groups in the ^{1}H NMR spectrum.

The basic system **3** inserted the olefin with a preference toward primary over secondary insertion, but was less efficient in the regiochemical control. **2** and **4**, containing the more acid moiety P(3-$CF_3C_6H_4$)$_2$, displayed a higher selectivity for the primary insertion over the secondary. Total regio- and stereocontrol was achieved with **2**. **4** afforded one primary insertion products and a mixture of the two secondary insertion products in comparable amount (M^{II}:m^{II} *ca.* 1.4:1).

As far as the complexes modified with C_s-symmetrical ligands are concerned, the insertion products have different stability and their distributions can be explained in terms of *trans* influence control, as in the case of CO insertion into metal-alkyl complexes [21]. **2** afforded one primary insertion product with the alkyl group *trans* to the P(3-$CF_3C_6H_4$)$_2$. The same stereochemical control was observed for the only primary insertion product identified for **4**. Also in the case of **3** the main primary insertion product M^I presented the alkyl group *trans* to the more acidic moiety PPh_2.

Steric reasons may explain the prevalence of primary to secondary insertion for all the systems investigated. In the secondary insertion the methyl group of propene undergoes stronger steric repulsion due to aryl substituents of the phosphorus, while in the primary insertion it is exposed to a less hindered environment. The overall product distribution suggests that an isomerization pathway is very likely for each insertion mode. The major isomer in the palladium acyl complex presents the acyl group *trans* to the more electron-withdrawing moiety of the ligand. Upon propene insertion, the primary insertion product M^I presents the alkyl group *trans* to the more electron-withdrawing moiety in the case of **2** and **4** ($PdCH_2$ *trans* to P(3-$CF_3C_6H_4$)$_2$), where only one stereoisomer is formed, and in the case of **3** ($PdCH_2$ *trans* to PPh_2), where two stereoisomers in ratio 1.5:1 are observed. For **3** and **4** the ratio between the secondary insertion products is 1:1 and *ca.* 1.4:1, respectively. The ratios of the isomers and the competition primary/secondary insertion indicate a combination of electronic and steric effects in the regio- and stereocontrol of propene insertion. Conversely, the stereocontrol in ethene insertion appears to be driven by steric factors, as the closely equimolar distribution of the products is formed with the more electron-rich ligand **3**, as well as with the more electronic-withdrawing system **2**.

Propene insertion into a palladium acyl complex modified with a phosphine-imine ligand has been recently reported [21]. Upon treatment with propene, two products were formed in ratio 1:1. Although not explicitly mentioned in the work reported, propene insertion into the palladium imine phosphine complex should lead to a good stereochemical control, with the formation of only one kind of stereoisomer (*i.e.*, the product with the alkyl group *trans* to the imine and *cis* to the phosphine), but displayed no regiochemical control as the two modes were equally accessible. The systems investigated in this work displayed a higher degree of regiocontrol with the prevalence of primary over secondary insertion.

In comparison with propene insertion into Pd complexes containing BINAPHOS, an efficient stereocontrol was achieved, with the preferential location of the alkyl group *trans* to the more electron-withdrawing moiety of the ligand. Regiocontrol was sometimes not so high (case of the ligands **3** and **4**) with a maximum overall ratio primary: secondary insertion of 3.7:1 (systems containing **4**).

4. Conclusions

Insertion of ethene was investigated for the systems **2** and **3**. Irrespective of the electronic character, the insertion afforded the equimolar mixture of the two stereoisomers in both cases. This suggests that electronic factors are not so crucial for the insertion of ethene in this kind of complexes. Steric factors have been proposed to play the major role in the reactivity toward olefins [45].

Propene insertion into the stereoisomeric mixture of the acyl complexes modified with C_s-symmetric diphosphine ligands **2–4** and the parent ligand **1** were investigated. **1**, the reference compound, formed one primary insertion product. Among the C_s-symmetric ligands investigated, **2** displayed the higher stereo- and regioselectivity. Upon propene insertion only one stereoisomer was formed, bearing the alkyl group *trans* to the $P(3\text{-}CF_3C_6H_4)_2$ moiety, which corresponded to a primary insertion product. In the case of **4**, three products resulted from propene insertion. The ratio between 1,2- and 2,1-insertion products was 3.7:1. The species afforded by primary insertion bore the alkyl group *trans* to the more acid moiety $P(3\text{-}CF_3C_6H_4)_2$. The secondary insertion products were found in ratio *ca.* 1.4:1, but could not be completely characterized by NMR. For **3** four products were formed. The primary insertion and the secondary insertion products were formed in an overall ratio of 5.9:1. The two primary insertion products were formed in a ratio 1.5:1. The main stereoisomer of the primary insertion products, M^I, had the alkyl group *trans* to the more acidic moiety PPh_2 of the ligand. The 2,1-insertion products, which were formed in a ratio 1:1, could not be fully characterized by NMR. The stereoisomeric distribution can be rationalized to some extent by *trans* influence concept. The alkyl group with high *trans* influence receives better thermodynamic stabilization by locating *trans* to the less electron donating moiety of the ligand, as already observed for the CO insertion studies in the palladium-alkyl complexes [44].

The high regio- and stereocontrol observed in the copolymerization experiments suggest that isomerization pathways may take place at some point of the catalytic cycle. Contributions of the growing polymer chain may influence and differentiate the stability of the intermediates, lowering the energy of some defined reaction pathways. Only one intermediate may then be effective in controlling the stereo- and regioselectivity of the copolymerization.

5. Experimental part

The preparation of the palladium methyl-solvento complexes has been previously described elsewhere [44].

5.1. NMR spectroscopy

$CDCl_3$ was purchased from Dr. Glaser AG.

The ^1H, ^{13}C, $^{31}P\{^1H\}$, and 2D spectra were measured in $CDCl_3$ and recorded on a Bruker Avance 500 (frequency in MHz: ^1H, 500.13; ^{13}C, 125.77; ^{31}P, 202.45). Chemical shifts are given in parts per million (ppm) relative to TMS (internal standard) or the solvent residual peak for ^1H and ^{13}C NMR, and relative to 85% H_3PO_4 (external standard) for $^{31}P\{^1H\}$ NMR.

The coupling constants J are given in hertz. The multiplicity is denoted by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; qt, quintet; sx, sextet; sp, septet; m, multiplet; dd, doublet of doublets; dq, doublet of quartets; br, broad.

NMR probe temperature was measured by means of a thermocouple. Standard pulse sequences were employed for ^{13}C–^1H, ^{31}P–^1H, ^1H-TOCSY and ^1H-NOESY correlation studies. ^1H-TOCSY spectra were recorded using a 0.2 s mixing time. ^1H-NOESY spectra were recorded using a 0.8 s mixing time.

5.2. Olefin insertion study

From a 20–25 mg of the complex $[PdCH_3(P^\wedge P')(CH_3CN)](OTf)$ ($P^\wedge P$ = **1–4**) in $CDCl_3$, the acyl complex was generated *in situ* by bubbling CO or ^{13}CO for 5–10 min at −60 °C. The temperature of the solution was raised from −60 °C to −20 °C and 25–28 equivalents of the olefin (ethene, propene) were introduced into the NMR tube by means of a gastight syringe. The sample was inserted into a precooled (−20 °C) NMR probe and the spectra were acquired at that temperature. Attempts to isolate the insertion products resulted in the decomposition of the adducts and formation of Pd(0). Deconvolution of the NMR spectra was performed using the Bruker software WINNMR.

Carbon monoxide (purity grade 4.7) was purchased from Pan Gas. ^{13}CO (^{13}C, 99%) was purchased from Cambridge Isotope Laboratories. Propene (purity grade 2.8) and ethene (purity grade 3.5) were purchased from Linde.

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