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Influence of ligands and anions on the insertion of alkenes into palladium–acyl and palladium–carbomethoxy bonds in the neutral complex (dppp)Pd(C(O)CH_3)Cl and the ionic complexes [(P–P)PdR(L)]$^+$$SO_3CF_3^-$ (P–P = dppe, dppp, dppb; R = C(O)CH_3, L = CH_3CN, PPh_3; R = C(O)OCH_3, L = PPh_3)

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Abstract

Insertions of alkenes in Pd–acetyl bonds of (dppp)Pd(C(O)CH_3)Cl and [(P–P)Pd(C(O)CH_3)L)]$^+$ $SO_3CF_3^-$ (P–P = dppe, dppp, dppb; L = CH_3CN, PPh_3) have been studied as a function of the ligand, the anion and the alkene. The neutral acetyl complex (dppp)Pd(C(O)CH_3)Cl underwent insertion only with norbornadiene and norbornene, while the ionic acetyl complexes [(P–P)Pd(C(O)CH_3)(L)]$^+$ $SO_3CF_3^-$ (P–P = dppe, dppp, dppb) reacted with norbornadiene, norbornene, styrene, *cis*-stilbene, 1-pentene, 3,3-dimethyl-1-butene, vinyltrimethylsilane, methyl vinyl ketone, methyl acrylate, diethyl fumarate, and diethyl maleate. The insertion was observed to give an intermediate in which there was intramolecular coordination of the ketone oxygen atom to the palladium centre. In monosubstituted alkenes the acetyl group migrates to the unsubstituted carbon atom. The insertion products underwent β-elimination to give (*trans*) unsaturated ketones and a palladium hydride. The rate of this elimination was higher for complexes containing ligands L–L with smaller bite angles (dppe > dppp), and the rate of insertion showed the reverse order. The carbomethoxy complexes [(P–P)Pd(C(O)OCH_3)(PPh_3)]$^+$ $SO_3CF_3^-$ (P–P = dppe, dppp, dppb) were prepared from (P–P)Pd(SO_3CF_3)$_2$ with CO, CH_3OH and PPh_3. The carbomethoxy complex reacted with norbornadiene to give a carbomethoxy oxgyen-coordinated intermediate. The carbomethoxy complexes were less reactive than the analogous acetyl complexes towards alkenes.

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Introduction

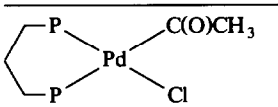
The copolymerization of ethene and carbon monoxide has been the subject of industrial research for quite some time [1]. It was appreciated that the alternating copolymer with a melting point well above 200°C and mechanical strength comparable with nylon type polymers would be commercially very attractive in view of the low cost of the starting materials. An efficient catalyst was lacking for a long time. The relatively low yields of polymer per gram of catalyst yielded a material that was intrinsically unstable owing to the presence of catalyst residues in the polymer. A breakthrough was achieved about a decade ago by Drent and coworkers who found that palladium complexes with bidentate phosphines as the ligands are excellent catalysts for the alternate copolymerization of alkenes and carbon monoxide [2]. The advantages of that system are the minimal loss of catalyst and the high turnover rates. The polymerization process involves initiation reactions, insertion or chain growth reactions and, since the synthesis of more than one chain per palladium atom is highly desirable, chain transfer reactions. We have investigated two of these steps of the catalytic cycle, *i.e.* carbon monoxide insertion into metal–alkyl bonds and alkene insertions into metal–acetyl bonds and metal–carbalkoxy bonds. The reports of the studies of the carbon monoxide insertion will be published elsewhere [3,4].

Insertion of carbon monoxide into metal–alkyl bonds has been thoroughly studied for a variety of metal complexes [5]. Insertions of alkenes into metal-hydrides and metal-alkyl complexes have also been much studied. By contrast, very few studies have been devoted to the insertion of alkenes into metal-acyl bonds. The insertion into metal–carbon bonds was thought to occur by a process similar to that for the insertion in metal–hydride bonds, albeit with a higher barrier of activation [6]. Sen and Brumbaugh [7–10] studied the insertion of norbornene and norbornadiene into palladium-acyl complexes with *monodentate* phosphine ligands and their results are pertinent to ours. Reaction of *trans*-$(PPh_3)_2PdCl(COR)$ with norbornene produced $(PPh_3)PdCl(C_7H_{10}COR)$ with intramolecular coordination of the ketone oxygen atom. The reaction was faster in the presence of complexing reagents for triphenylphosphine. The same authors reported on the copolymerization of ethene and carbon monoxide using the same complexes with monodentate ligands, their studies giving the most detailed information to date on the copolymerization [11]. Copolymerization of CO and alkenes with the complex $[(PPh_3)_nPd(CH_3CN)_{4-n}](BF_4)_2$ ($n = 1$–3) as the catalyst showed alkene insertion to be the rate-determining step [7]. The effectiveness of the termination of the polymerization chain by alcohols was shown to be dependent on the bulk of the alcohol and on its nucleophilicity. It was also shown that the electrophilicity of the metal was of little importance compared with the availability of a vacant site at the metal centre [10]. Insertion of alkenes into metal–carbomethoxy bonds, which may be relevant to polyketone formation, is one of the mechanistic pathways for the alkoxycarbonylation of alkenes, as recently shown by Milstein [12].

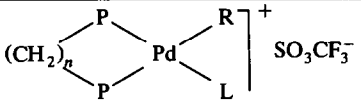
Following Drent's reports on the use of diphosphines for palladium-catalysed carbonylation reactions interest in this field has grown strongly [13]. In a recent study of the carbonylation of alkenes catalyzed by ionic complexes $[(dppp)Pd(solvent)_2](X)_2$ (dppp = 1,3-bis(diphenylphosphino)propane; X = non- or weakly-coordinating anion) it was found that under hydroformylation conditions

Table 1

Numbering of the complexes used in the insertions of alkenes



(1)



R L	$C(O)CH_3$ $L = CH_3CN$	$C(O)CH_3$ $L = PPh_3$	$C(O)OCH_3$ $L = PPh_3$
$Ph_2P(CH_2)_2PPh_2$ (dppe)	**2a**		**4a**
$Ph_2P(CH_2)_3PPh_2$ (dppp)	**2b**	**3**	**4b**
$Ph_2P(CH_2)_4PPh_2$ (dppb)	**2c**		**4c**

(160 bar CO/H_2 1:1, 77°C) the reaction with styrene produced 1,5-diphenylpentan-3-one and *E*-1,5-diphenylpent-1-en-3-one in a ratio of 5:95 with ~99% selectivity [14]. No polymerization was reported and no intermediates were detected.

In this paper we present the results of the study of insertions of several alkenes into the palladium–acetyl bonds in complexes (dppp)Pd($C(O)CH_3$)Cl and [(P–P)Pd($C(O)CH_3$)(CH_3CN)]$^+SO_3CF_3^-$ (P–P = 1,2-bis(diphenylphosphino)-ethane (dppe), dppp, 1,4-bis(diphenylphosphino)butane (dppb)). The mechanism of alkene insertion is discussed together with the influence of the diphosphine ligands and of the steric and electronic properties of the alkenes on the rate and regioselectivity of the insertion. The insertion of alkenes into the palladium–acyl bonds in [(P–P)Pd($C(O)CH_3$)(CH_3CN)]$^+SO_3CF_3^-$ and in [(dppp)Pd($C(O)CH_3$)-(PPh_3)]$^+SO_3CF_3^-$ is compared with that of insertion into the palladium-carbomethoxy bond in the complexes [(P–P)Pd($C(O)OCH_3$)(PPh_3)]$^+SO_3CF_3^-$ (P–P = dppe, dppp, dppb).

Results

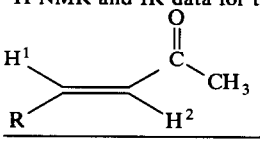
The preparations of the palladium-acyl complexes **1**, **2a–c**, and **3** have been described previously. The numbering of the complexes used in this paper is shown in Table 1.

Reaction of (dppp)Pd($C(O)CH_3$)Cl (1) with alkenes

Reaction of 1 with norbornadiene and norbornene. Reaction of **1** with norbornadiene resulted in immediate quantitative formation of two new complexes, which showed ^{31}P resonances at 27.5/−5.2 ppm (^2J(P–P) = 64 Hz) and at 25.8/−4.7 ppm (^2J(P–P) = 65 Hz). The latter complex was the major species present. The $^{31}P\{^1H\}$ NMR data for both complexes point to the formation of a palladium–alkyl species; the chemical shift and the coupling constant ^2J(P–P) in the $^{31}P\{^1H\}$ NMR spectra are diagnostic for the presence of a palladium–alkyl– or a palladium–acyl complex [3]. When the reaction was performed at 243 K only one complex was observed, with resonances at 27.7/−5.8 ppm (^2J(P–P) = 65 Hz) in the $^{31}P\{^1H\}$ NMR spectrum. The ^1H NMR spectrum showed multiplets at 5.2 ppm and at 5.8 ppm due to inequivalent olefinic hydrogen atoms. In the low-frequency region of the ^1H NMR spectrum only the $C(O)CH_3$ resonance could be distinguished. The

Table 2

^{1}H NMR and IR data for the observed organic β-elimination/decomposition products



Reacting alkene	^{1}H NMR (ppm)				IR (cm^{-1})
	CH_3	R	H^1 [a]	H^2 [a]	ν(CO)
Norbornadiene [b,c]	2.18	0.8–3.3m	6.6m; 6.3m	–	1705
Norbornene [b]	2.18	1.0–2.4m	6.86d [3]	–	1695
Styrene	2.38	6.9–8.0m	6.70d [17]	[d]	1665; 1610
3,3-Dimethyl-1-butene	2.24	1.08	5.94d [16]	6.77d [16]	1710
1-Pentene	2.11	0.8–1.3m 2.0–2.8m	6.05d [15]	6.73d [15]	1705
Vinyltrimethylsilane	2.26	0.05	5.9 [13]	6.3 [13]	1720
Methyl acrylate	2.31	3.76	6.62d [16]	7.00d [16]	1710; 1690
Methyl vinyl ketone	2.16		6.8 [b]		1710

[a] $^3J(H\text{–}H)_{trans}$ in square brackets. [b] H^2 not present, R represents full organic skeleton. [c] As a mixture of *exo*- and nortricyclenyl. [d] Obscured by aromatic protons of ligand (and alkene); m: multiplet; d: doublet.

change in the $C(O)CH_3$ shift from 1.90 ppm (**1**) to 2.40 ppm as well as the lowering of the IR frequency from 1690 in **1** to 1620 cm^{-1} are consistent with coordination of the ketone oxygen atom to the palladium centre. Intramolecular ketone coordination has been observed before [10,15]. After one day the insertion products had decomposed into the organic products listed in Table 2 and to unidentified low-valent palladium complexes. Norbornene reacted instantaneously with **1** to form only one complex, with absorptions at 27.5 and −5.8 ppm (^2J(P–P) = 64 Hz) in the $^{31}P\{^1H\}$ NMR spectrum. The ^{1}H NMR spectrum showed a singlet at 2.28 ppm due to the $C(O)CH_3$ group of the insertion product, while the olefinic hydrogen resonance at 5.99 ppm had disappeared. The IR spectrum showed a band at 1620 cm^{-1}.

There are two explanations for the formation of two products from norbornadiene (Fig. 1): (*i*) *exo* and *endo* attack on one of the norbornadiene olefinic bonds, giving two 2,3-insertion products; and (*ii*) formation of one 2,3-insertion product, together with the 2,6-insertion with concomitant formation of the 3,5-bond to give a nortricyclenyl product.

Insertion of norbornadiene and norbornene into the palladium-acyl bond in $(PPh_3)_2Pd(C(O)CH_3)Cl$ was reported by Brumbaugh *et al.* [10]. The X-ray struc-

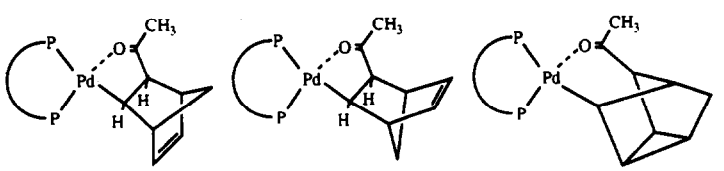


Fig. 1. Three different kinds of norbornadiene insertion into the Pd–$C(O)CH_3$ bond: *exo*- and *endo*-insertion and nortricyclenyl formation.

ture of *exo-exo*-$(PPh_3)_2Pd$(2-acetyl-1-norborn-1-yl), the insertion product from norbornene, showed that the substitution at the alkene had taken place at the *exo* face. A nortricyclenyl product was reported to be formed in the phenylation of (η^4-norbornadiene)Pd complexes [16]. More recently, formation of a nortricyclenyl product was shown to be catalyzed by a Pd–phosphine system [17]. In view of these results and the fact that norbornene in our case also gives only one product it is concluded that norbornadiene leads to a mixture of *exo* and nortricyclenyl insertion products (explanation *ii*). It therefore seems that when attack takes place at the *endo* face this leads to the nortricyclenyl product. The intramolecular coordination of the ketone group *via* its oxygen atom to the Pd centre indicates that Cl^- is displaced. We cannot say whether Cl^- is fully dissociated or is coordinated at the apical position.

Norbornene reacted similarly (see above), giving only the *exo* product with the ketone oxygen coordinated to the Pd centre. After 30 minutes a secondary product appeared at 13.1 and −9.9 ppm (^2J(P–P) = 78 Hz) (^{31}P). In the IR spectrum a broad absorption at 1700 cm^{-1} was observed. The shifts and the large coupling constant in the $^{31}P\{^1H\}$ NMR spectrum point to formation of a new palladium–acyl complex [3] due to insertion of a second CO molecule. The broad absorption at 1700 cm^{-1} might be due to overlap of the absorptions of the new Pd–C(O)R group and the non-coordinating ketone $C(O)CH_3$ group, which are both expected to have an absorption near 1700 cm^{-1}. Deinsertion and multiple insertion reactions are notorious for obstructing the study of these processes [10]. Brumbaugh reported the formation of cyclopentyl cyclopentenyl ketone in the reaction of an acetyl palladium complex with cyclopentene, and that can only be explained in terms of multiple insertion reactions at palladium [10]. In the case of cationic species (see below) multiple insertions are not observed; ketone coordination stabilizes the primary product. It is argued that, after the second insertion has taken place, Cl^- coordination shifts the equilibrium to the right (a > b), as depicted in Fig. 2 (L=Cl^-), and thus Cl^- coordination makes up for the loss of carbonyl oxygen coordination. After 12 hours decomposition of the insertion product had occurred (Table 2).

Reaction of 1 with cyclohexene, cyclopentene, styrene, methyl acrylate, 3,3-dimethyl-1-butene and methyl vinyl ketone. Cyclohexene, cyclopentene, styrene, methyl acrylate, 3,3-dimethyl-1-butene and methyl vinyl ketone underwent no reaction with **1** during 3 days at 25°C; after that time over 60% of the palladium-acyl complex had decomposed.

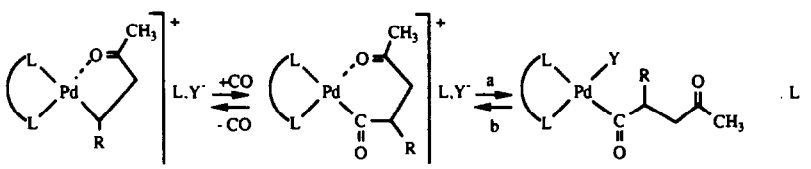
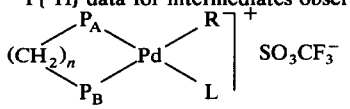


Fig. 2. Equilibria in the insertion of alkenes into the palladium–acyl bond. For $Y^- = Cl^-$, L = solvent: a > b. For $Y^- = SO_3CF_3^-$, L=CH_3CN: b > a.

Table 3

$^{31}P\{^1H\}$ data for intermediates observed in the alkene insertion into complexes **2a–c** and **3**



Reacting alkene	**2a**	**2b**	**2c**	**3**
	$\delta/\delta^a[^2J(P-P)]$	$\delta/\delta^a[^2J(P-P)]$	$\delta/\delta^a[^2J(P-P)]$	$\delta/\delta^a[^2J(P-P)]$
Norbornadiene	55.4/36.0 [36] [b]	25.3/−5.6 [64] [b]	43.5/2.0 [50] [b]	25.5/−5.0 [64] [b]
	56.1/33.8 [37]	27.4/−6.2 [63]	44.7/2.6 [51]	27.4/−5.6 [63]
Norbornene		27.4/−6.0 [64]		
Styrene	54.5/44.0 [44]	17.8/3.4 [76]	28.3/13.7 [57]	17.7/3.2 [77]
cis-Stilbene		n.o.		
trans-Stilbene		n.r.		
1-Pentene		28.5/−4.3 [56]		
3,3-Dimethyl-1-butene	61.2/39.2 [28]	11.45/−5.55 [c]		
Vinyltrimethylsilane		26.9/−4.3 [56]		
Methyl vinyl ketone	58.7/48.8 [29]	22.4/−1.4 [58]	n.o.	
Methyl acrylate	59.3/44.5 [29]	23.1/−2.3 [56]	38.8/6.9 [46]	23.2/−2.4 [56]
Diethyl maleate	61.8/47.6 [28]	24.3/−1.5 [56]		
Diethyl fumarate	61.5/47.1 [27]	25.0/−1.7 [55]		
2a–c [3]	40.2/30.9 [47]	10.1/−4.9 [80]	13.6 and 13.3	20.3/−4.9/−7.2 [e]
(ref. Pd-alkyl [d])[3]	61.3/38.7 [28]	27.0/−3.7 [54]	34.7/16.4 [41]	[65]/[−230]/[47] [f]
			22.6 and 22.2	34.9/−2.3/13.2 [e]
				[55]/[−361]/[36] [f]

[a] First δ mentioned is P_A, the second δ is P_B [3]. [b] Major species present. [c] Second order pattern of an AA'XX' system, with $J_{AX} = -60$, $J_{AA'} = 5$, $J_{XX'} = 200$ and $J_{AX'} = 115$ Hz (revealed from simulation of the spectrum, see Experimental). [d] Pd–CH_3 complex as precursor for the Pd–$C(O)CH_3$ complex. [e] First two δ's: P_A and P_B, third δ: L = PPh_3 [3]. [f] $^2J(P_A-P_B)$, $^2J(P_A-PPh_3)$ and $^2J(P_B-PPh_3)$ respectively. n.o.: not observed; n.r.: no reaction.

Reaction of complexes [(P–P)Pd(C(O)CH$_3$)(CH$_3$CN)]$^+$SO$_3$CF$_3^-$ (2a–c) with alkenes

The reactivity of a variety of alkenes towards the ionic complex [(dppp)Pd-(C(O)CH$_3$)(CH$_3$CN)]$^+$SO$_3$CF$_3^-$ (**2b**) was studied. The dppp complex was chosen because complexes containing this ligand had shown the highest reactivity thus far; (dppe)Pd(CH$_3$)Cl and [(dppe)Pd(CH$_3$)(CH$_3$CN)]$^+$SO$_3$CF$_3^-$ had already shown a low reactivity towards CO. The dppb complexes give oligomeric species [(dppb)Pd(R)(CH$_3$CN)]$_n^{n+}$(SO$_3$CF$_3^-$)$_n$ ($n \geq 2$; R = CH$_3$, C(O)CH$_3$) [3] which may hamper the analysis of the complexes formed. Nevertheless, a selection of substrates were treated with the complexes **2a** and **2c**. $^{31}P\{^1H\}$ NMR spectra of the intermediates observed are listed in Table 3.

Reaction of 2a–c with norbornadiene and norbornene. Treatment of **2a** and **2b** with norbornadiene resulted in immediate formation of two complexes, while **2c** reacted during 15 min, also to yield two complexes (Table 3). In the ^1H NMR spectrum the oxygen-coordinated C(O)CH$_3$ group of the insertion product was observed at 2.61 (**2a**), 2.37 (**2b**) and 2.43 (**2c**) ppm, and two broad multiplets of the inequivalent olefinic hydrogens were observed at 5.5 and 5.9 ppm (**2a**) and at 5.2 and 5.8 ppm (**2b** and **2c**). The IR spectra showed an absorption at 1620 cm^{-1} (the starting complexes **2a–c** show an absorption at 1690 cm^{-1} [3]).

Reaction of **2b** with norbornene immediately yielded one complex (Table 3). The ^{1}H NMR spectrum showed a new singlet at 2.30 ppm due to the $C(O)CH_3$ group of the insertion product. The IR spectrum showed an absorption at 1620 cm^{-1}.

On the basis of the similarity of the IR and NMR data we suggest that the reactions of both norbornadiene and norbornene lead to the same complexes as were formed on the reactions with the neutral palladium-acetyl complex **1**, *i.e.* involving the intramolecular ketone oxygen coordination to the Pd centre.

As stated above, in the reaction of the cationic complex **2b** with norbornene there is no secondary insertion of CO. The intramolecular coordination of the ketone in a five-membered ring is particularly stable in both **1** and **2b**. In contrast to stabilization of **1**, by the Cl^- anion, coordination of the $SO_3CF_3^-$ anion does not stabilize the secondary CO insertion product. As a result the product of the thermoneutral insertion reaction of CO is not observed in the case of **2b** (b > a) (Fig. 2).

Reaction of 2a–c with styrene, cis- *and* trans-*stilbene.* Styrene reacted within 10 min with **2a** and **2b** to give one complex (Table 3). Reaction with **2c** was much slower, only 60% of **2c** reacting in 24 hours. The ^{1}H NMR spectrum showed new singlets at 2.35 ppm (**2a**), 1.75 ppm (**2b**) and 2.40 ppm (**2c**) assigned to the $C(O)CH_3$ group. For **2b** the signals from the $C(O)CH_3$ group appeared at a rather low frequency. Further, multiplets were observed at 3.63 ppm (^2J(H,H) = 10 Hz; ^3J(H,H) = 3.5 Hz) and 3.1 ppm (no fine structure could be analyzed) (**2b**). For **2a** one broad multiplet was observed at 3.6 ppm; the other could not be seen because of overlap with the resonances of the CH_2 groups of the dppe backbone. The IR spectrum obtained immediately after addition of styrene to **2a–c** showed a broad absorption at 1710–1720 cm^{-1} which we assign to an insertion product in which the carbonyl oxygen is not intramolecularly coordinated to the metal. The phosphorus resonances, the magnitude of the coupling constant ^2J(P–P), and the IR frequency of the $C(O)CH_3$ group may indicate an η^3-coordination of the benzylic product of insertion, as depicted in Fig. 3.

The η^3-coordination will change the P–Pd–P angle and hence the coupling constant ^2J(P–P) is changed together with the shifts of the phosphorus resonances. Similar shifts of the phosphorus resonances were found in the reaction of styrene with $[(dppp)Pd(H)(PPh_3)]^+SO_3CF_3^-$ in the absence of CO [18].

The shift of the $C(O)CH_3$ resonance for the insertion product from **2a** and **2c** is significantly different from that of the product from **2b**. The differences in the shifts of the $C(O)CH_3$ resonances may be due to the proximity of one of the phenyl groups of the ligand [19]. The multiplets observed at 3.63 ppm and 3.1 ppm

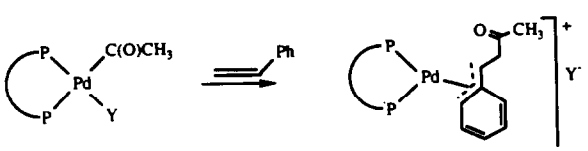


Fig. 3. Possible formation of an allylic intermediate after insertion of styrene into the Pd–$C(O)CH_3$ bond in $[(P–P)Pd(C(O)CH_3)(CH_3CN)]^+ SO_3CF_3^-$.

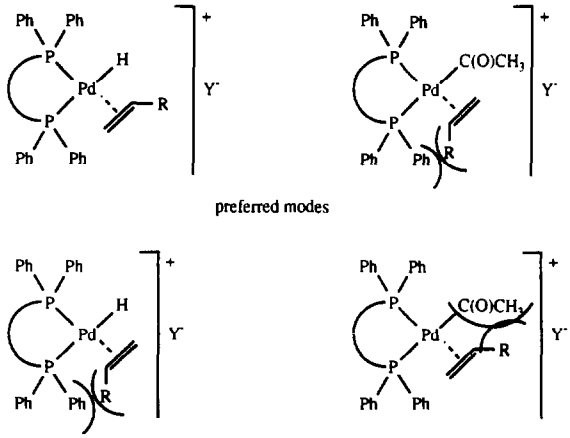


Fig. 4. Effect of the sterical hindrance on the stereochemistry of insertion of an alkene into a Pd–H bond and into a Pd–$C(O)CH_3$ bond.

(**2b**) and 3.6 ppm (**2a**) are assigned to the allylic protons. The high frequency multiplets are assigned to the protons attached to the phenyl-substituted carbon.

The insertion of styrene involves attack of the acetyl group at the β-carbon of styrene, as indicated by the formation of a 1,2-*trans* β-elimination product. It has been reported that the catalytic reaction of styrene with a Pd complex in the presence of CO results in the formation of *E*-1,5-diphenyl-1-penten-3-one [14]. The product is formed by subsequent insertion of styrene into a palladium–hydride bond, insertion of CO into the palladium–alkyl formed, and insertion of styrene into the new palladium–acyl bond and β-elimination. The difference in regioselectivity between the insertion into the palladium–hydride bond and the palladium–acyl bond has presumably a steric origin. In the first step the hydride attacks at the α-carbon of styrene, but the acyl formed after insertion of CO attacks the second molecule of styrene at the β-carbon atom, as in our reaction. Figure 4 shows how the steric properties govern the regioselectivity of the two steps.

In the course of the reaction multiplets of low intensity were also observed at 1.34 ppm (**2a**), 1.0 ppm (**2b**) and 0.85 ppm (**2c**) in the ^1H NMR spectrum; no new $^{31}P\{^1H\}$ NMR resonances could be distinguished. These resonances are assigned to insertion of styrene in a Pd–H complex. The Pd–H complex is formed together with an α,β-unsaturated ketone via β-elimination from the insertion products of **2a–c**. After 12 hours (**2a**) or 2 days (**2b**) the β-elimination was complete, while for **2c** this product was already formed before the insertion reaction was complete (Table 2).

For *cis*-stilbene no insertion complexes were observed in the $^{31}P\{^1H\}$ NMR spectra. The ^1H NMR spectrum shows the isomerization of *cis*-stilbene (6.58 ppm) to *trans*-stilbene (7.11 ppm). Isomerization of several alkenes have been reported to be catalyzed by cationic species such as $[Pd(CH_3CN)_4](BF_4)_2$ [20] or $[(dppe)Pd(\mu\text{-}OH)]_2(BF_4)_2$ [21].

trans-Stilbene did not show any reaction with **2b** during 3 days; after that time over 60% of the palladium–acyl complex had decomposed.

Reaction of 2a–c with 3,3-dimethyl-1-butene, vinyltrimethylsilane and 1-pentene. Complex **2a** reacted with 3,3-dimethyl-1-butene during 1 hour, to give one complex (Table 3). After 3 hours the reaction mixture from complex **2b** showed a second order pattern in the $^{31}P\{^1H\}$ NMR spectrum of the dark red solution (Table 3), while no insertion product was observed in the $^{31}P\{^1H\}$ NMR spectrum. Simulation of the spectrum (see Experimental) revealed the presence of an AA'XX' system, with the approximate coupling constants $J_{AX} = -60$ Hz, $J_{AA'} = 5$ Hz, $J_{XX'} = 200$ Hz and $J_{AX'} = 115$ Hz matching perfectly with the observed spectrum. The system proved to be identical to the dimeric Pd(I)–Pd(I) species $[(dppp)Pd]_2^{2+}(SO_3CF_3^-)_2$, which was recently structurally characterized [22a; see also 22b]. The dimer may be formed by aggregation of Pd–H complexes with evolution of H_2 or via reaction of Pd^0 with Pd^{II} species, both reactions being possible after β-elimination of the organic insertion product. Formation of the β-elimination product (Table 2) was complete within 3 hours for both **2a** and **2b**. Complex **2c** did not react during 4 days.

The reaction of 1-pentene with **2b** gave no clear information; the solution was red after 15 min and the second order pattern ($^{31}P\{^1H\}$ NMR) of $[(dppp)Pd]_2^{2+}$ could be distinguished. The ^1H NMR and IR spectra of the reaction mixture showed only signals assigned to the β-elimination product (Table 2).

Vinyltrimethylsilane reacted immediately with **2b** to give one complex (Table 3), which was the result of an insertion ($^{31}P\{^1H\}$ NMR). The ^1H NMR spectrum showed resonances at 2.18 and -0.03 ppm and the IR absorption of the $C(O)CH_3$ group appeared at 1675 cm^{-1}. We assign these data to an insertion product in which the carbonyl oxygen atom is not coordinated to the metal. Almost immediately after addition of vinyltrimethylsilane to the palladium–acyl complex the solution turned red. The β-elimination of the organic product (Table 2) was complete in 12 hours.

Reaction of 2a–c with methyl vinyl ketone, methyl acrylate, diethyl maleate, and diethyl fumarate. Reaction of methyl vinyl ketone with **2b** resulted in the immediate formation of a single complex (Table 3), **2a** reacted in 30 min to give one complex (Table 3), while **2c** showed no reaction. The ^1H NMR spectrum showed two singlets of equal intensity at 2.66 (**2a**) and 2.28 ppm (**2b**) ($C(O)CH_3$ group coordinating via the oxygen atom) and at 1.23 (**2a**) and 1.54 ppm (**2b**) (non-coordinating $C(O)CH_3$ group), and IR absorptions were observed at 1625 and 1710 cm^{-1} for the coordinating and non-coordinating $C(O)CH_3$ groups, respectively. In the case of **2a** quantitative decomposition to Pd^0 occurred during 4 hours. After 12 hours the $^{31}P\{^1H\}$ NMR spectrum of the dark red solution of **2b** showed a complicated pattern, among which the second order pattern of $[(dppp)Pd]_2^{2+}$ could be distinguished. After 4 days the reaction mixture of **2c** showed the presence of the same organic β-elimination product as was observed for the reaction with **2a** and **2b** (Table 2), but no intermediate insertion products were observed.

Reaction of **2a** and **2b** with methyl acrylate gave within 10 minutes a single complex, whereas in the case of **2c** only 50% had reacted after 24 hours (Table 3). In the ^1H NMR spectrum singlets were observed at 3.19 ppm (**2a**), 3.24 ppm (**2b**) and 3.21 ppm (**2c**) ($C(O)OCH_3$ group) together with singlets at 2.60 ppm (**2a**), 2.35 ppm (**2b**) and 2.41 ppm (**2c**) (oxygen coordinating $C(O)CH_3$ group). The IR spectrum showed absorptions at 1675 (both **2a** and **2b**) and 1625 cm^{-1} (**2a**) and

1630 cm^{-1} (**2b**), the last two being indicative of intramolecular coordination of the ketone group. Addition of CO or PPh_3 to the reaction mixture after insertion caused no change in the spectra. The organic β-elimination product (Table 2) was gradually formed in 4 days (**2a**), 10 days (**2b**), or during the reaction (**2c**).

In the reactions of both **2a** and **2b** with diethyl maleate two insertion products were formed. The same insertion products were also formed in the reactions with a mixture of diethyl maleate/diethyl fumarate (Table 3). We suggest that partial isomerization of diethyl maleate to diethyl fumarate takes place [21]. The ^1H NMR spectrum showed singlets at 2.70 ppm (**2a**) and 2.41 ppm (**2b**) and singlets of lower intensity at 2.42 ppm (**2a**) and 2.28 ppm (**2b**) for the products of the reaction with diethyl maleate and that with the diethyl maleate/diethyl fumarate mixture. For both insertion complexes of **2a** and **2b** the ethyl groups give signals at 0.66 and 0.73 ppm (CH_3) and 4.25 and 3.98 ppm (CH_2) with coupling constants $^3J(H,H)$ of 7 Hz. In the reaction with **2b** the olefinic hydrogen resonances of both diethyl maleate and diethyl fumarate decreased in intensity, while for **2a** the decrease of the diethyl maleate olefinic resonance was stronger than that of diethyl fumarate. The overall rate of insertion of diethyl maleate was higher for **2b** than for **2a**. These observations strongly suggest that diethyl maleate is more reactive than diethyl fumarate towards **2a** due to steric constraints. The overlapping signals of ligand and substrate do not allow any conclusion concerning the stereochemistry of the insertion product.

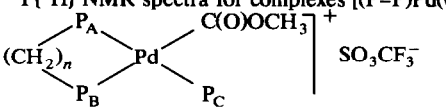
The strong resemblance of the $^{31}P\{^1H\}$ NMR spectrum of the methyl acrylate reaction with the spectra of the diester alkene reactions indicates that in all reactions stable complexes are formed with similar structures. This suggests that in the products of the reactions with the diesters the ketone-oxygen atom is coordinated to the Pd centre rather than the ester-oxygen atom. The stability of the products in the reaction of the ester and the diester substituted alkenes is probably due to the electron-withdrawing groups at the α-carbon bonded to the Pd centre. The product in the reaction of **2b** with methyl acrylate did not react with CO, and this may be explained as follows. First, the ester group makes the α-carbon of the migrating group less nucleophilic. Secondly, CO coordination is suppressed by the intramolecular ketone coordination. An alternative to this kinetic interpretation is that the intramolecular carbonyl coordination has such a strong stabilizing effect that CO insertion is thermodynamically unfavourable.

Reaction of $[(dppp)Pd(C(O)CH_3)(PPh_3)]^+SO_3CF_3^-$ (3) with alkenes

Complex **3** reacted instantaneously with norbornadiene, whereas 1 hour was needed for methyl acrylate and 5 hours for styrene. The $^{31}P\{^1H\}$ and ^1H NMR spectra of the insertion products formed were the same as these observed for the reaction of **2b** with norbornadiene, methyl acrylate and styrene (Table 3). The IR spectrum of the reaction mixture in the case of norbornadiene showed an absorption at 1620 cm^{-1}, indicating that the coordinating PPh_3 group is replaced by the carbonyl oxygen atom. This is corroborated by the $^{31}P\{^1H\}$ NMR spectrum, which shows the spectrum of a bidentate coordinated phosphine (Table 3) and free PPh_3. The lower rates for **3** relative to **2b** (especially for methyl acrylate and styrene) are ascribed to the stronger coordination of PPh_3 relative to CH_3CN.

Table 4

$^{31}P\{^1H\}$ NMR spectra for complexes $[(P-P)Pd(C(O)OCH_3)(PPh_3)]^+SO_3CF_3^-$ (**4a–c**)



Compound	$\delta(P_A)$	$\delta(P_B)$	$\delta(P_C)$	$^2J(P_A-P_B)$	$^2J(P_A-P_C)$	$^2J(P_B-P_C)$
4a [a]	46.5	40.7	18.8	30	−306	28
4b [a]	−3.6	−4.5	20.9	56	−305	35
4c [a]	3.2	16.5	23.3	40	−298	37

[a] In $CH_3OH/CH(OCH_3)_3$(4/1). The ^{31}P shifts of the precursor Pd-complexes in CD_2Cl_2 are given: (dppe)$Pd(SO_3CF_3)_2$: 75.4 ppm; (dppp)$Pd(SO_3CF_3)_2$: 17.6 ppm; (dppb)$Pd(SO_3CF_3)_2$: 49.2 ppm.

*Formation of $[(P\text{-}P)Pd(C(O)OCH_3)(PPh_3)]^+SO_3CF_3^-$ complexes **4a–c** and their reactivity towards alkenes*

In the reaction between $(P-P)Pd(SO_3CF_3)_2$ (P–P = dppe, dppp, dppb) and CO in the presence of CH_3OH and an additional ligand, PPh_3, the complexes palladium-carbomethoxy complexes $[(P-P)Pd(C(O)OCH_3)(PPh_3)]^+SO_3CF_3^-$ (Table 4) were formed [23].

The presence of PPh_3 is necessary to avoid decomposition of the palladium–carbomethoxy complex. Furthermore, it is necessary to work in solutions free from water in order to prevent formation of the Pd–H complex $(dppp)Pd(H)SO_3CF_3$ via a shift reaction. For this purpose 20% v/v of trimethyl orthoformate ($CH(OCH_3)_3$) was added since this effectively removes water from acidic solutions of methanol [24]. A few similar palladium-carbomethoxy complexes have been previously reported [12,25,26].

In the case of the reactions of **4a–c** with alkenes only $^{31}P\{^1H\}$ NMR spectra were obtained. No ^1H NMR spectra could be obtained because of the presence of the large excess of CH_3OH and $CH(OCH_3)_3$. Complexes **4a–c** underwent no reaction with styrene or methyl acrylate during 5 days. Norbornadiene reacted with **4a**, **4b** and **4c** to give insertion products resembling those formed in the reactions of **2a**, **2b** and **2c** with norbornadiene (Tables 5 and 3 respectively).

PPh_3 did not coordinate to palladium in the insertion product, as shown by the $^{31}P\{^1H\}$ NMR spectra. We suggest that coordination of the ester-oxygen atom to the Pd centre occurs in the same way as ketone-oxygen coordination. Other complexes with intramolecular ester coordination to palladium have been reported

Table 5

$^{31}P\{^1H\}$ data for intermediates observed in the alkene insertion into complexes **4a–c**

Reacting alkene	**4a**	**4b**	**4c**
	δ/δ [a] $[^2J(P-P)]$	δ/δ [a] $[^2J(P-P)]$	δ/δ [a] $[^2J(P-P)]$
Norbornadiene	60.1/33.7 [34]	28.2/−5.8 [63]	45.1/−0.5 [52]
	57.2/35.0 [34]	27.0/−4.8 [64]	44.3/−0.7 [52]
Methyl acrylate	n.r.	n.r.	n.r.
Styrene	n.r.	n.r.	n.r.

[a] First δ mentioned is P *trans* to L (see Table 3), and the second δ is P *trans* to organic group (see Table 3). n.r.: no reaction.

[27]. Complex **4b** did not react with methyl acrylate or styrene. In a study concerning the hydrocarbalkoxylation of alkenes catalyzed by palladium complexes it was reported that 1-hexene did not insert into the palladium–carbomethoxy bond of *trans*-$(PPh_3)_2PdCl(C(O)OCH_3)$ [26].

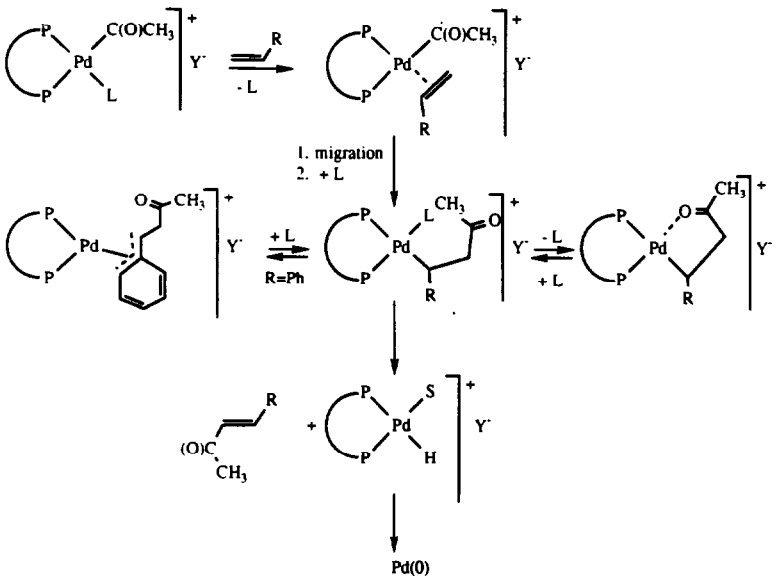
Discussion

Influence of bidentate ligands on the insertion

The rate of insertion of the alkenes into the palladium–acyl bonds studied falls in the order **2b** ≥ **2a** > **2c**. The low reactivity of the dppb complex **2c** is ascribed to the *trans* configuration of the oligomeric acyl complexes. When insertion did take place, as with norbornadiene, the strong carbonyl coordination resulted in formation of the monomeric *cis* insertion complex similar to those formed from **2a** and **2b**. The difference between **2b** and **2a** is more subtle, as only a few alkenes insert, at a higher rate for **2b** than for **2a**. Insertion of carbon monoxide into palladium–methyl bonds is faster into dppp complexes than into dppe complexes [3]. This can be attributed to the higher flexibility of the dppp backbone. Extended Hückel and *ab initio* calculations [6,28] on the insertion of ethene in the platinum–hydride bond of *cis*-$(PH_3)_2Pt(H)(C_2H_4)$ have shown that the opening of the P–Pt–P angle during the insertion lowers the energy of the process. Coordination of the alkene in a position cis to the metal–hydride bond is necessary for insertion and the alkene and the platinum–hydride bond have to be co-planar [6]. The necessity of this arrangement in the square plane was recently questioned; insertion via a five-coordinate intermediate was proposed for intramolecular insertion reactions at Pt [29] and five-coordinate species were also invoked for CO insertions into palladium–phenyl bonds [30].

The insertion products from **2a** underwent faster β-elimination than those from **2b**. Recently, it was reported that in the complexes $[(P–P)Pt(C_2H_5)]^+$ (P–P = $(^tBu)_2P(CH_2)_2P(^tBu)_2$ (dbpe), $(^tBu)_2P(CH_2)_3P(^tBu)_2$ (dbpp), *o*-$((^tBu)_2PCH_2)_2$-C_6H_4 (dbpx)) β-hydrogen elimination is favoured when the diphosphine contains shorter bridges; in the dbpe complex β-hydrogen elimination was found, while in the dbpp and dbpx complexes agostic interactions were observed [31]. The series dbpe, dbpp and dbpx is similar to the series dppe, dppp and dppb: in each set there are 2, 3, and 4 carbon atoms, respectively, in the backbone. The authors stated that the size of the ligands (including the effect of the bite angle of the bidentate) determines the tendency towards β-elimination, smaller ligands giving alkene-hydride species through β-elimination and larger ligands giving alkyl species with agostic interaction. If insertion is kinetically enhanced by larger bite angles (*vide supra*) one would expect that on the basis of microscopic reversibility deinsertion (β-elimination) would also be accelerated by more flexible ligands (dppp > dppe). The present results indicate that thermodynamic stabilities of the complexes must contribute to the observed ligand effects on insertion and β-elimination.

For a polymerisation process it is desirable to promote insertion reactions, and suppress β-elimination reactions, and hence, dppp-containing complexes are clearly the most attractive species [2].



Scheme 1. Reaction scheme for the insertion of alkenes into the palladium–acyl bond ($Y^- = Cl^-$ or $SO_3CF_3^-$, in the latter case also CH_3CN present).

Influence of anions, additional ligands and the migrating group on the insertion

The rate of alkene insertion in the palladium-acyl complexes falls in the order $[(dppp)Pd(C(O)CH_3)(CH_3CN)]^+SO_3CF_3^-$ (**2b**) ≫ $[(dppp)Pd(C(O)CH_3)(PPh_3)]^+SO_3CF_3^-$ (**3**) ≫ $(dppp)Pd(C(O)CH_3)Cl$ (**1**), which points to the need for an easily accessible site for the insertion reaction of alkenes.

The spectra of the insertion products of **1**, **2b** and **3** with norbornadiene and norbornene are identical, which means that Cl^- (**1**), CH_3CN (**2b**) and PPh_3 (**3**) are all dissociated in the insertion product. These observations indicate that the intramolecular ketone–oxygen coordination is fairly strong. The overall process of insertion of alkene and β-elimination is shown in Scheme 1.

The higher reactivity of the palladium-acetyl complex **3** relative to the palladium-carbomethoxy complex **4b** is ascribed to the higher nucleophilicity of the acetyl group than of the carbomethoxy group.

Alkene reactivity

It is generally accepted that migration involves nucleophilic attack by the migrating group on the alkene [32]. Hence, a positive charge and/or a low lying LUMO of the alkene will increase the ease of migration. On the basis of their LUMO levels, the reactivities of the alkenes are expected to decrease in the order: *cis*- and *trans*-stilbene, methyl acrylate, diethyl fumarate, diethyl maleate, methyl vinyl ketone > styrene > norbornadiene > vinyltrimethylsilane > norbornene > 3,3-dimethyl-1-butene > 1-pentene > cyclohexene > cyclopentene. Steric crowding results in the following order of decreasing reactivity of the alkenes: monosubstituted alkene > disubstituted *cis*-alkene > disubstituted *trans*-alkene.

In the present work, the observed reactivities were found to decrease in the order: norbornadiene, norbornene > methyl acrylate, diethyl maleate, methyl vinyl

ketone, vinyltrimethylsilane, 1-pentene > styrene > 3,3-dimethyl-1-butene > *cis*-stilbene, diethyl fumarate > *trans*-stilbene. This order shows the electronic effects to be of less importance than strain and steric effects. Only within a series of equal steric hindrance do the electronic properties become important.

Experimental section

All reactions and manipulations were carried out under purified nitrogen by use of Schlenk techniques. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Bruker AC 100 spectrometer at 100.13 MHz and 40.53 MHz, respectively. Shifts are relative to $(CH_3)_4Si$ (^{1}H) and 85% H_3PO_4 (^{31}P) as external standards, with positive shifts to high frequency. Simulations of the spectra were carried out at the Koninklijke/Shell-Laboratorium Amsterdam with the program geNMR, version 3.1 (IvorySoft, Amsterdam, 1989). IR spectra were recorded with a Perkin–Elmer 283 spectrometer. CH_2Cl_2 was dried over P_2O_5. Benzene, diethyl ether and pentane were dried over Na-wire. All solvents were distilled from the respective desiccants and stored under nitrogen. All liquid alkenes were filtered over basic Al_2O_3, in order to remove oxidized species and stabilizing agents, prior to use. Preparation of complexes **1**, **2a–c** and **3** is described elsewhere [3]. Silver trifluoromethanesulfonate ($AgSO_3CF_3$) and trimethyl orthoformate ($CH(OCH_3)_3$ were obtained from Janssen Chimica. The complexes (dppe)$PdCl_2$, (dppp)$PdCl_2$ and (dppb)$PdCl_2$ were made by published methods [33].

(dppe)Pd(SO_3CF_3)$_2$. To a suspension of (dppe)$PdCl_2$ (0.74 g, 1.29 mmol) in 15 mL of THF were added 2 equivalents of $AgSO_3CF_3$(0.66 g, 2.58 mmol). After 24 h the solution was filtered and evaporated in vacuum. The resulting yellow powder was recrystallized from a mixture of CH_2Cl_2/diethyl ether. The yield was 0.63 g (61%) of yellow powder. Anal. Found: C, 41.75; H, 2.98; P, 7.35. $C_{28}H_{24}P_2S_2O_6F_6Pd$ calcd.: C, 41.88; H, 3.01; P, 7.71%.

(dppp)Pd(SO_3CF_3)$_2$ and (dppb)Pd(SO_3CF_3)$_2$. The same procedure was used as for the preparation of (dppe)Pd(SO_3CF_3)$_2$, except that (dppp)$PdCl_2$ and (dppb)$PdCl_2$ were used instead of (dppe)$PdCl_2$. Anal. Found: C, 42.20; H, 3.27; P, 6.99. $C_{29}H_{26}P_2S_2O_6F_6Pd$ ((dppp)Pd(SO_3CF_3)$_2$) calcd.: C, 42.63; H, 3.21; P, 7.58%, yield: 74% of yellow powder. Found: C, 43.28; H, 3.58; P, 7.24. $C_{30}H_{28}P_2S_2O_6F_6Pd$ ((dppb)Pd(SO_3CF_3)$_2$): calcd.: C, 43.36; H, 3.40; P, 7.45%, yield: 58% of yellow powder.

*(dppe)Pd(C(O)OCH_3)(PPh_3)(SO_3CF_3) (**4a**).* A gentle stream of CO (*ca.* 40 mL/min) was passed for 3 min through a solution of (dppe)Pd(SO_3CF_3)$_2$ (0.051 g, 0.064 mmol) and PPh_3 (0.017 g, 0.064 mmol) in 0.5 mL of a mixture of CH_3OH and $CH(OCH_3)_3$ (9:1) in an NMR tube. After addition of CD_2Cl_2 (0.25 mL) the $^{31}P\{^{1}H\}$ NMR spectrum showed that complex **4a** had been formed quantitatively. Attempts to isolate the product were unsuccessful due to decarbonylation and/or decomposition.

*(dppp)Pd(C(O)OCH_3)(PPh_3)(SO_3CF_3) (**4b**) and (dppb)Pd(C(O)OCH_3)(PPh_3)(SO_3CF_3) (**4c**).* The procedure for the preparation of **4a** was used but with (dppp)Pd(SO_3CF_3)$_2$ and (dppb)Pd(SO_3CF_3)$_2$ in place of (dppe)Pd(SO_3CF_3)$_2$.

Alkene insertion into palladium-acyl bonds in complexes 1, 2a–c and 3 and into palladium–carbomethoxy bonds in complexes 4a–c. One equivalent of alkene was added into a solution containing the palladium–acetyl or the palladium–

carbomethoxy complex (1 mmol in 0.5 mL CD_2Cl_2). The mixture was shaken and the ^1H and $^{31}P\{^1H\}$NMR spectra were recorded, the first spectrum being obtained after 3 minutes. Spectra were taken after 3, 8, 15, 25, 40, 60, 90, 120 and 180 min and after 12 h, 1, 2, 4, 8 days. Owing to gradual decomposition during the reaction no organopalladium products could be isolated.

HOMO and LUMO levels (in eV). HOMO: norbornadiene 8.42 [34], norbornene 8.81 [35], *trans*-stilbene 7.95, *cis*-stilbene 7.95, methyl vinyl ketone 10.10 [36], styrene 8.43 [37], 1-pentene 9.52, 3,3-dimethyl-1-butene 9.7 [38], vinyltrimethylsilane 9.8 [39], methyl acrylate 10.72, diethyl maleate 10.47, diethyl fumarate 10.70 [40]. LUMO: *trans*-stilbene ≈ 0, *cis*-stilbene ≈ 0 [41], styrene -0.25 [42], norbornadiene -1.04 [43], norbornene -1.70 [44], 1-pentene -1.92 [45], 3,3-dimethyl-1-butene -1.73, vinyltrimethylsilane -1.15 [46]. For methyl vinyl ketone, methyl acrylate, diethyl maleate, and diethyl fumarate no values for the LUMO levels were found; they were estimated to be between those for stilbene and styrene.

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