Chemistry of palladium phosphinite ($PPh_2(OR)$) and phosphonite ($P(OPh)_2(OH)$) complexes: catalytic activity in methoxycarbonylation and Heck coupling reactions

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The new phosphinite and phosphonite complexes (**1–8**) are very efficient catalysts for the methoxycarbonylation of iodobenzene and Heck cross-coupling of bromobenzene with butyl acrylate. High catalytic activity of these complexes can be explained by their *in situ* transformations during the reaction, stimulated by the presence of water, acid (HCl) or base (NEt_3). Hydrolysis of phosphinite palladium complexes of the form *trans*-$PdCl_2[PPh_2(OR)]_2$ (R = C_6F_5 **2**, ${}^tBu$ **3**, or O-menthyl **4**) results in the formation of the dimeric complex [μ-ClPd(PPh_2OH)(PPh_2O)]$_2$ **5**, which is deprotonated by NEt_3, producing a polymeric complex of formula $[Pd(P(O)PPh_2)_2]_n$ **8**. The reverse reaction, protonolysis of **8** with HCl, leads back to **5** and the monomeric complex **5a**. The phosphinite complex $PdCl_2[PPh_2(OBu)]_2$ **1** with a more lipophilic ligand, $PPh_2(OBu)$, does not undergo hydrolysis under the same conditions. In the reaction of PdCl$_2$(cod) with $P(OPh)_2(OH)$, the new dimer [μ-ClPd($P(OPh)_2OH$)($P(OPh)_2O$)]$_2$ **6** was obtained, whereas reaction of $Pd(OAc)_2$ with $P(OPh)_2(OH)$ leads to the polymeric complex $[Pd[P(O)(OPh)_2]_2]_n$ **7**. Protonolysis of **7** with HCl results in the formation of **6**.

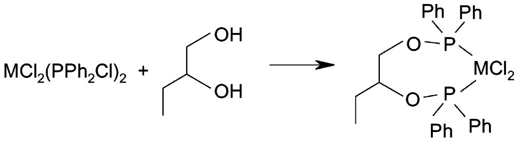
Introduction

Phosphinites ($PPh_2(OR)$) and hydrogen phosphonates ($HP(O)(OR)_2$) represent an interesting alternative to phosphines as ligands for metal ions used as catalysts in organic synthesis. Their practical application in catalytic systems is however complicated by sensitivity towards hydrolysis, leading to a change in the ligand and catalyst structure. This report demonstrates an improvement in catalytic activity as a result of such transformations initiated by the presence of water as well as HCl or NEt_3.

Phosphinites as free ligands can be easily prepared in the reaction of PPh_2Cl with alcohols or diols (eqn (1)).[1,2]

$$PPh_2Cl + ROH \rightarrow PPh_2(OR) + HCl \quad (1)$$

Alternatively, phosphinites, specifically vicinal diphenylphosphinites, can be synthesized through metal template synthesis, as has been demonstrated for reactions of $MCl_2(PPh_2Cl)_2$ complexes (M = Pd, Pt) with diols, leading to square planar complexes containing chelating diphosphinite (eqn (2)).[3,4]



(2)

Metal template synthesis is particularly useful for the preparation of optically active derivatives which can then be used as catalysts in chiral synthesis. Recently, several applications of such catalysts have been reported, mainly for the enantioselective formation of C–C and C–heteroatom bonds through allylic substitution reactions.[5–9] A palladium complex with phosphinite-oxazoline ligands derived from D-glucosamine worked efficiently in asymmetric allylic substitution.[5] Good results, represented by high ee values, have also been obtained in this reaction with a palladium catalyst containing furanoside thioether-phosphinite,[6] aminophosphonites,[7] as well as N,P-donor oxazoline phosphinites.[8,9] Surprisingly, in spite of their generally higher air-stability compared to phosphines, phosphinites have seldom been used in palladium-catalyzed C–C bond forming reactions, such as methoxycarbonylation of aryl halides or Heck or Suzuki coupling. Catalytic systems containing $Pd(dba)_2$ and PPh_2(O-menthyl) or aminophosphine phosphinite have been used in the carbonylation of α-methylbenzyl bromide under phase-transfer conditions but exhibited low activity and poor optical yield compared to aminophosphine or 2-substituted-3,1,2-oxazaphospholanes.[10] Another example of the application of phosphinite palladium complexes in carbonylation reactions, although a non-asymmetric one, has been published by us.[11] It was found that the yield of phenylacetic acid methyl ester formed by methoxycarbonylation of benzyl bromide depends on the structure of the phosphinite ligand coordinated to palladium in the $PdCl_2P_2$ complex, and generally better results were obtained with ligands with less steric hindrance (P = $PPh_2(OMe)$, $PPh_2(OBu)$).[11] The activity of palladium phosphinite complexes in Heck and Suzuki reactions has been illustrated mostly by complexes with phosphinite PCP pincer ligands. A phosphinito palladium PCP pincer complex efficiently catalyzed Heck coupling of aryl chlorides with styrene at 120–180 °C.[12] Suzuki coupling of aryl bromides with a bis(phosphinite) PCP pincer palladium complex[13] and with P,C-bidentate phosphinite palladacycles[14] have been performed successfully. A palladium complex with a hemilabile amino- and sulfur-containing phosphinite ligand has been found to catalyze the Heck reaction of aryl bromides with styrene at 130 °C, with high turnover numbers and a good selectivity towards *trans*-stilbenes.[15] An

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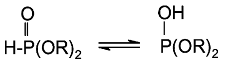
air-stable phosphinite ligand, $P(^tBu)_2(OH)$, has been found as an ideal ligand for palladium catalysts for a variety of C–C, C–N, and C–S bond forming reactions,[16] also with aryl chlorides as substrates.[17,18] Arylation of 2,3-dihydrofuran using a palladium complex with a phosphinite-oxazoline ligand originating from D-glucosamine proceeded smoothly to give 78–96% ee; however, it gave lower ee in enantioselective phenylation of *cis*- and *trans*-crotyl alcohols.[19] A supported phosphinite ligand obtained from a polymer-bound aminoalcohol template reacted with $Pd(OAc)_2$ and the obtained complex was used in the Heck reaction.[20]

The role of hydrolytic transformations of phosphinites under Suzuki reaction conditions with orthometallated palladium phosphinito complexes as catalysts has been found to be important and dependent on the kind of ligand and palladium precursor.[13]

It has been discovered that $PPh_2(OH)$ (in the form $HP(O)Ph_2$) can be coupled with alkynes in hydrophosphinylation reactions catalyzed by palladium complexes.[21,22] In a similar application, hydrophosphorylation of alkenes and alkynes leading to phosphonate derivatives, hydrogen phosphonates existing in two tautomeric forms have been found (eqn (3)).[23–25]



$$\mathrm{H\text{-}P(=O)(OR)_2 \rightleftharpoons HO\text{-}P(OR)_2} \qquad (3)$$

Simple substrates such as $HP(O)(OR)_2$ (R = alkyl, aryl) are often unreactive, but the addition of α-pinacol-derived hydrogen phosphonate to a variety of olefins in the presence of palladium complexes has been successful.[24,25] Palladium-catalyzed hydrophosphorylation of alkynes with $HP(O)(OEt)_2$ and $HP(O)(OMe)_2$ has also been reported.[23] The formation of $MeP(O)(OPh)_2$ by reductive elimination from palladium complexes of the type $L_2PdMe(P(O)(OPh)_2)$ (L = $PMePh_2$, PMe_2Ph, PEt_3 *etc.*), a key step in P(O)–C(sp^3) bond forming reactions, has been investigated, and the effect of steric properties of the ligand L on the reaction rate has been demonstrated.[26,27]

During our earlier studies on the catalytic activity of palladium phosphinite complexes in the methoxycarbonylation of benzyl bromide, we observed that some of these complexes were unstable in solution, and their recrystallization was seriously complicated by unidentified structural changes.[11] It seemed interesting to investigate and explain the nature of those transformations and to determine their influence on the catalytic activity of the systems. Literature data concerning the catalytic activity of palladium complexes with monodentate phosphinites are rather scarce, and even less is known about the catalytic applications of palladium phosphonate complexes, which have been tested only in phosphorylation reactions.[23–25] Therefore, we chose to study not only methoxycarbonylation but also the Heck reaction (Scheme 1). Both reactions proceed in the presence of base, acting as scavengers of HX formed as a side product and therefore, the catalyst should suffer basic as well as acidic conditions without decomposition. The studies of reactions of palladium phosphinito and phosphonato complexes with NEt_3 and HCl has allowed the determination of the stability of catalysts.

The important part of these studies is related to the elementary steps of the catalytic processes, common to both reactions (Scheme 1), namely reactions of Pd-catalyst precursors with NEt_3, representing the base present in both catalytic systems. The eventual reduction of Pd(II) to Pd(0) with contributions from amine was expected, just as has been reported for $PdCl_2[P(OPh)_3]_2$ (eqn (4)).[28]

$$\mathrm{PdCl_2P_2 + N(C_2H_5)_3 + H_2O \rightarrow [Pd^0] + 2\,HCl + CH_3CHO} \\ \mathrm{+HN(C_2H_5)_2 + 2\,P} \qquad (4)$$

$$\mathrm{P = P(OPh)_3}$$

$PdCl_2[P(OPh)_3]_2$ reacted with NEt_3 in the presence of H_2O with the formation of a Pd(0) complex according to reaction (4).[28]

Results and discussion

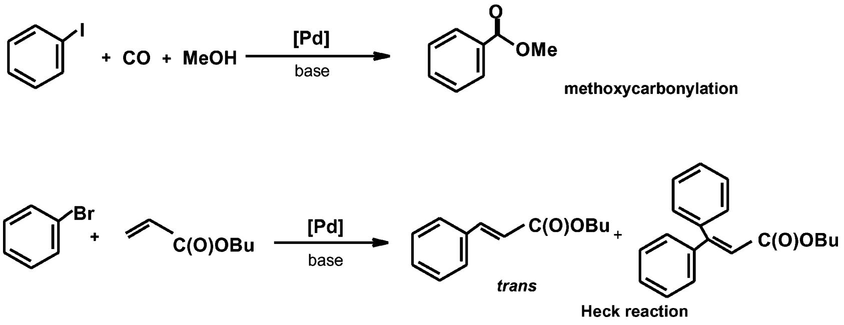
Hydrolysis of Pd(II) phosphinite complexes of the type $PdCl_2[PPh_2(OR)]_2$ (2–4)

The phosphinito palladium(II) complexes selected for these studies, of the $PdCl_2P_2$ type (P = $PPh_2(OR)$), can be divided into *cis* and *trans* isomers depending on the steric hindrance of the phosphinite ligand[11] (Scheme 2). Only $PdCl_2[PPh_2(O^nBu)]_2$ **1** forms a *cis* isomer, and for a phosphorus ligand P = $PPh_2(C_6F_5)$ **2**, $PPh_2(O^tBu)$ **3**, or PPh_2(O-menthyl) **4**, the formation of *trans* isomers was confirmed.[11] The structure of the complexes was determined from spectroscopic data, and in the case of **4**, preliminary X-ray data indicated *trans* coordination of phosphinite ligands, but the quality of the crystals was not sufficient to resolve the final structure.

$PdCl_2[PPh_2(OR)]_2$

R =	isomer	complex
^{n}Bu	cis	1
C_6F_5	trans	2
^{t}Bu	trans	3
menthyl	trans	4

Scheme 2



Scheme 1 Methoxycarbonylation and Heck reaction patterns.

During the measurements of ^{31}P NMR spectra of palladium(II) phosphinite complexes **2**, **3**, and **4** in solution, it was observed that all the complexes were transformed to the same compound **5** with a characteristic signal at 78 ppm.

The new compound was detected after one hour in a solution of incompletely dried $CDCl_3$. The observed position of the signal in the ^{31}P NMR spectrum (78 ppm) is similar to that reported in the literature (78.1 ppm) for the dimer **5** of formula $[\mu\text{-ClPd}(PPh_2OH)(PPh_2O)]_2$;[3,29] however, very similar data (79.6 ppm) have also been published for monomeric *cis*-$PdCl_2[PPh_2(OH)]_2$,[13] complex **5a**.

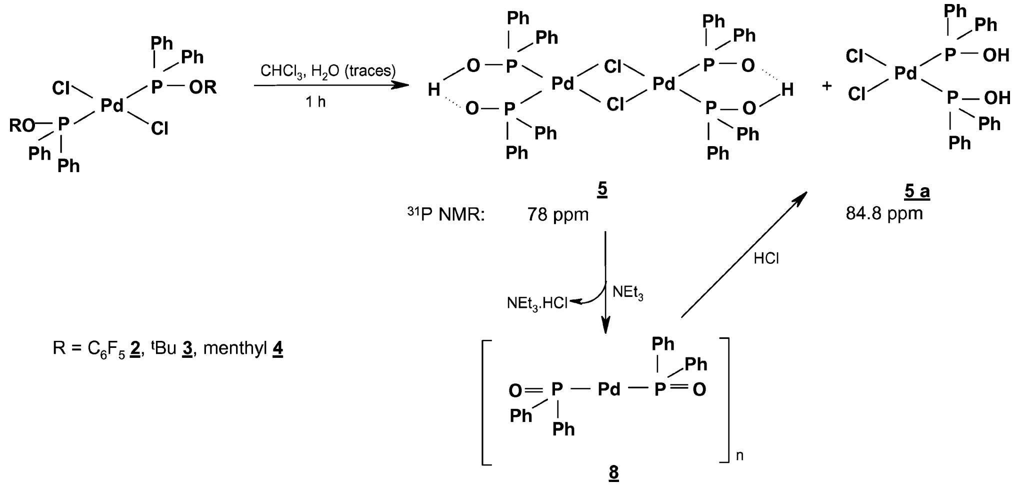
To determine which structure, dimeric **5** or monomeric **5a**, is correct, complexes **2** and **4** were recrystallized respectively from a mixture of $CHCl_3$ with EtOH and from only C_6H_6, and the obtained crystals were analyzed by X-ray crystallography. The complex, which recrystallized from a $CHCl_3$ and EtOH mixture, was identified as the dimer **5** with 2 molecules of $CHCl_3$ in the lattice, identical with that described in ref. 29 (Scheme 3). The process of the formation of **5** in ref. 29 was based on the reaction of the phosphinite complex *cis*-$PdCl_2[PPh_2OCH_2)_2\cdot{}^{n}BuCl_x$ (where $^{n}BuCl_x$ is tetra-n-butoxycalix[4]arene) with HCl. The dimer **5** was also been obtained earlier from the reaction of $PdCl_4^{2-}$ with $PPh_2(OH)$.[30] The recrystallization of **4** from C_6H_6 produced the same dimer **5** with one molecule of benzene in the crystal lattice (Fig. 1, Tables 1, 2). It is interesting to note that palladium phosphinite complexes undergo hydrolysis even with traces of water but not solvolysis in ethanol solution, and in consequence the formation of a palladium complex with the expected solvolysis product, $PPh_2(OEt)$, was not proved experimentally.

By analogy to the pathway proposed for the hydrolysis of phosphites,[30] the reaction of a phosphinite complex with water is presented in Scheme 4. Such a reaction of complexes **2**, **3**, or **4**

Table 1 Bond lengths (Å) and angles (°) in **5**[a]

Pd(1)–P(1)	2.2461(5)	Pd(1)–Cl(1)#1	2.4216(4)
Pd(1)–P(2)	2.2499(5)	Cl(1)–Pd(1)#1	2.4216(4)
Pd(1)–Cl(1)	2.4166(4)		
P(1)–Pd(1)–P(2)	91.789(17)	P(2)–Pd(1)–Cl(1)#1	90.615(16)
P(1)–Pd(1)–Cl(1)	92.973(16)	Cl(1)–Pd(1)–Cl(1)#1	84.701(16)
P(2)–Pd(1)–Cl(1)	174.768(16)	Pd(1)–Cl(1)–Pd(1)#1	95.299(16)
P(1)–Pd(1)–Cl(1)#1	176.917(17)		

[a] Symmetry transformation #1 −*x*, −*y*, −*z* defines center of symmetry located in position 0,0,0.



Scheme 3 Hydrolysis of phosphinite palladium complexes and their reactions with NEt_3 and HCl.

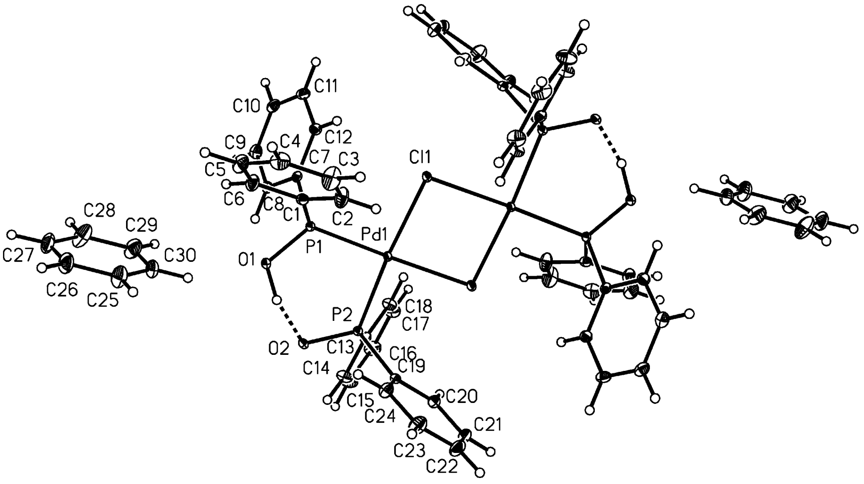
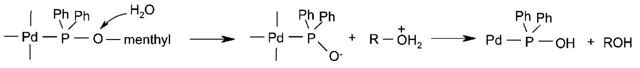


Fig. 1 Molecular view of $[\mu\text{-ClPd}(PPh_2OH)(PPh_2O)]_2$, **5**.

Table 2 Hydrogen-bonds for **5** [(Å) and angles (°)]

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
O(1)–H(1)···O(2)	1.04(3)	1.39(3)	2.4058(17)	164(3)

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y$, $-z$.



Scheme 4 Hydrolysis of Pd–phosphinite complex.

would provide complex **5a**, which eventually formed the dimer **5** after the release of two HCl molecules per 1 mol of the dimer **5**.

Transformation of complex **4** to the dimer **5** was examined with great care to elucidate the reaction mechanism. Comparison of ^1H NMR spectra (in the region 0–2 ppm) of complex **4** with those of menthyl alcohol and free phosphinite PPh_2(O-menthyl) led to the conclusion that the formation of menthyl alcohol, identified by the doublet of the CH_3 group at 0.73 ppm, J(H–H) 7 Hz, *versus* a doublet at 0.4 ppm, J(H–H) 7 Hz, in **4**, was simultaneous with the formation of the dimer **5**. The formation of the monomeric complex **5a** as well as dissociation of the phosphinite ligand were not observed. The lack of phosphinite ligand dissociation made it possible to assume that hydrolysis proceeded without Pd–P bond breaking.

To better understand the equilibrium between complexes **5** and **5a**, an experiment described in ref. 3 was repeated, and reaction of *in situ* prepared complex *cis*-$PdCl_2(PPh_2Cl)_2$ (obtained in the reaction of $PdCl_2$(cod) with PPh_2Cl) with water was studied. The ^{31}P NMR spectrum of the isolated crude product showed only one signal at 76.8 ppm (close to that observed earlier at 78 ppm) confirming the presence of the dimer **5** only.

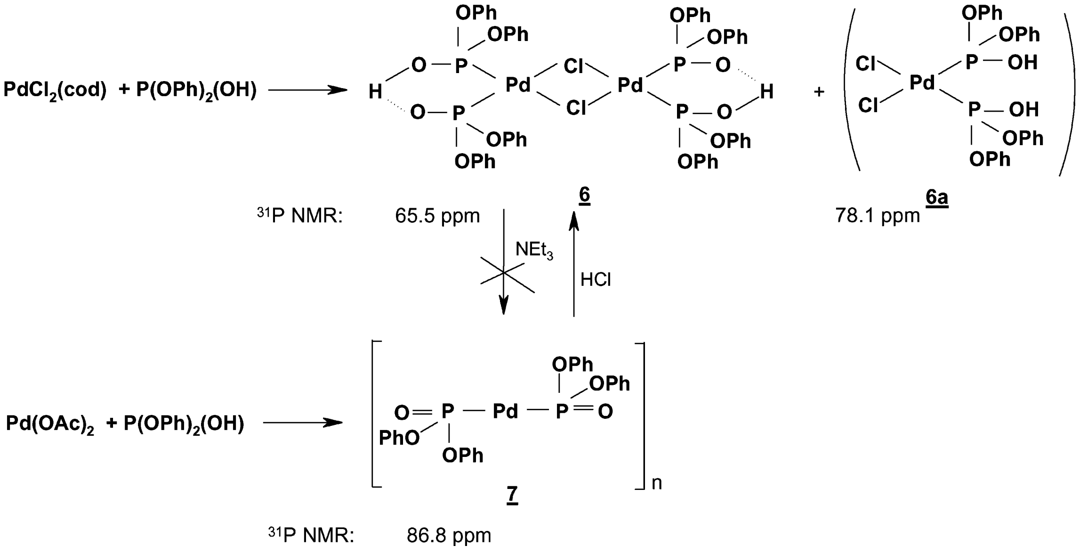
It is worth noting that, in contrast to the phosphinite complexes (**2**, **3**, **4**), complex **1** does not undergo hydrolysis, which may be explained by the difficult access for water molecules caused by the lipophilic character of the butoxy group. In the case of the remaining complexes, the attack of water molecules is facilitated by attraction of electron density from phosphorus by the R group in the PPh_2(OR) ligand.

Reactions of phosphinite palladium complexes (2–5) with NEt_3 and HCl

The experiments were performed in NMR tubes using a ten-fold excess of NEt_3 *versus* the palladium complex. A few minutes after the addition of NEt_3 to the solution of one of the complexes, **2**, **3**, **4**, or **5**, a precipitate of a new compound appeared in the tubes and was subsequently identified as the polymeric complex **8** containing $P(O)Ph_2^-$ anionic ligands coordinated to palladium (Scheme 3). This compound had been described earlier as the product of deprotonation of the dimer **5** after the addition of a base.[30] In our case NEt_3 played the role of a deprotonating agent that fixed HCl formed during the reaction. This was confirmed by the presence in the IR spectrum of frequencies characteristic for $NEt_3 \cdot HCl$ (2500, 2620, 2700 cm^{-1}). In the IR spectrum of **8**, a band at 1100 cm^{-1}, assigned to ν(P=O), was observed, whereas no bands in the region 200–400 cm^{-1}, corresponding to ν(Pd–Cl), were found. The very low solubility of **8** in common solvents does not make it possible to record its ^{31}P NMR spectrum. However, when a suspension of **8** in $CDCl_3$ was treated with a few drops of concentrated HCl in water, the mixture became clear, and its ^{31}P NMR spectrum presented two signals, at 76.8 ppm (the higher intensity) and at 84.9 ppm, due to the dimer **5** and the monomer **5a** respectively. It was the only case when we were able to see together both complexes, **5** and **5a**, in solution.

Formation of Pd–phosphonate complexes [μ-ClPd(P(OPh)$_2$OH)(P(OPh)$_2$O)]$_2$ 6 and [Pd[P(O)(OPh)$_2$]$_2$]$_n$ 7

The reactions of diphenyl phosphite $P(OPh)_2(OH)$ with $PdCl_2$(cod) and $Pd(OAc)_2$ were studied in solution using ^{31}P NMR spectrum measurements, and different products were found in each system (Scheme 5). When the $PdCl_2$(cod) complex reacted with a 2-fold excess of diphenyl phosphite, the evolution of the cod ligand was confirmed by the appearance of two singlets in ^1H NMR (2.36 and 5.59 ppm). In the ^{31}P NMR spectrum of the



Scheme 5 Reactions of palladium complexes with phosphonate ligands.

reacting solution recorded *in situ*, an intensive signal at 65.5 ppm and a much less intensive one at 78.1 ppm were observed. Further addition of $P(OPh)_2(OH)$ did not change the signal ratio, and only a free phosphite signal appeared at −2 ppm. In the ^{31}P NMR spectrum of the isolated solid palladium complex obtained in reaction of $PdCl_2$(cod) with $P(OPh)_2(OH)$ (Scheme 5), only one signal at 65.5 ppm was observed which was tentatively assigned to the dimer **6**. In the IR spectrum of complex **6**, two bands at 380.7 and 339.0 cm^{-1}, assigned to ν(Pd–Cl) stretching frequencies, were observed, and the dimeric structure **6** was supported by the presence of a peak at m/z 1184 in ESI-MS attributed to the $[M - Cl]^+$ fragment.

Reaction of $Pd(OAc)_2$ with $P(OPh)_2(OH)$ leads selectively to the formation of complex **7**, which has a polymeric structure with phosphonate ligands coordinating as $P(O)(OPh)_2^-$ anions. Such a structure of **7** is supported by the characteristic position of a ^{31}P NMR signal at 86.8 ppm due to the $P(O)(OPh)_2^-$ moiety[26] and the presence of an intensive IR band at 1100 cm^{-1} assigned to ν(P=O), which was not observed in the IR spectrum of **6**. The ^{31}P NMR spectrum of **7** was measured only *in situ*, in solution containing $Pd(OAc)_2$ and $P(OPh)_2(OH)$ ligands. It is worth noting that complex **7**, after having been isolated in the solid state, is insoluble in any available solvents used for NMR measurements and therefore its NMR spectra cannot be measured.

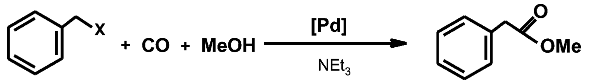
Attempts to transform the dimer **6** to the polymeric complex **7** by deprotonation with NEt_3, similar to the phosphinite complexes **5** and **8**, failed. When complex **6** in $CDCl_3$ was treated with NEt_3, some new signals appeared in the ^{31}P NMR spectrum of the solution in the region of 54–102 ppm, but a signal originating from complex **7** could not be found. Moreover, **7** can be easily transformed into **6** in a reaction with concentrated HCl, as was confirmed by the appearance of only one signal at 65.5 ppm in the ^{31}P NMR spectrum of a $CDCl_3$ solution obtained by treatment of the suspension of **7** with HCl.

The new route for the synthesis of palladium phosphonate complexes from $Pd(OAc)_2$ and $P(OPh)_2(OH)$ as substrates makes it possible to obtain products containing the $P(O)(OPh)_2^-$ anionic ligand with high selectivity. For comparison, recently a number of monomeric palladium complexes of the $Pd(Me)L_2(P(O)(OPh)_2)$ type have been described[26,27] which were obtained with the application of $AgP(O)(OPh)_2$ as the source of the phosphonate ligand.

Catalytic properties of palladium phosphinite and phosphonite complexes 1–8

Methoxycarbonylation of α-methylbenzyl bromide, benzyl bromide, and benzyl chloride catalyzed by 4. The obtained results confirmed the rather low catalytic activity of **4** in carbonylation of α-methylbenzyl bromide observed earlier,[10] despite different reaction conditions and different co-catalysts used. The yield of ester did not exceed 3% (at 60 °C, 5 atm CO), even in the presence of n-tetrabutyloammonium iodide as co-catalyst. Instead of ester, the main products were styrene and ether.

In spite of the very low activity of **4** in the carbonylation of α-methylbenzyl bromide, we checked its reactivity in the catalytic methoxycarbonylation of benzyl chloride and benzyl bromide (Scheme 6), and the yield of methyl phenylacetate obtained in these reactions is given in Table 3.



Scheme 6 Methoxycarbonylation of benzyl halides.

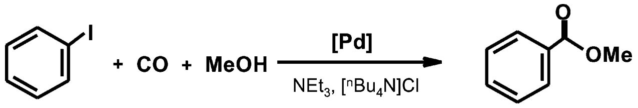
Table 3 Methoxycarbonylation of benzyl chloride and bromide catalyzed by **4**

Substrate $PhCH_2X$ (X =)	T/°C	p(CO)/atm	Co-catalyst	Yield of ester (%)
Cl	60	5	—	15
Br	40	1	—	27
Br	60	5	$[^nBu_4N]I$	41

Reaction conditions: [Pd] = 5 × 10^{-5} mol; $[PhCH_2X]$ = 9 × 10^{-3} mol; $[[^nBu_4N]I] : [PhCH_2X] = 1$; $[MeOH] : [PhCH_2X] = 8.3$; $[NEt_3] : [PhCH_2X] = 2.2$; 3 h.

Methoxycarbonylation of benzyl chloride compared with that of benzyl bromide required more stringent conditions. The yield of ester obtained from benzyl chloride in reaction catalyzed only by complex **4** at 60 °C, 5 atm CO for 3 h was 15%, whereas methoxycarbonylation of benzyl bromide gave 27% of ester at 40 °C under 1 atm CO. The addition of n-tetrabutyloammonium iodide made it possible to obtain 41% of ester. The positive effect of ammonium halides on the yield of methoxycarbonylation was also observed in other systems, and therefore further catalytic tests were performed in the presence of $[^nBu_4N]Cl$.

Methoxycarbonylation of iodobenzene catalyzed by complexes 1–8. To compare the catalytic activity of all of the studied palladium complexes (**1–8**), phosphinite and phosphonite ones, methoxycarbonylation reactions of iodobenzene were carried out under the same reaction conditions (90 °C, 5 atm CO) with ammonium salts as co-catalysts (Scheme 7).



Scheme 7 Methoxycarbonylation of iodobenzene.

It was expected that comparison of the obtained results would enable the determination of the impact of hydrolysis on the catalytic activity of the complexes under study and the relation between the molecular structure of the palladium complexes and their catalytic activity. Additionally, a comparison of the catalytic activity of phosphinite and phosphonite complexes could help in the estimation of the electronic effect of the respective phosphorus ligands on their reactivity.

Almost all of the palladium complexes under study presented high or very high catalytic activity in the test reaction: methoxycarbonylation of iodobenzene (the yield of methyl benzoate amounting to 66–100%, which corresponds to a TON of 400–600) (Table 4). The lowest yield of ester was obtained for complex **8** (46%), in contrast to 92% produced by the dimer **5**. This indicates that the transformation of **8** into **5**, which is quite fast in the presence of HCl, is not complete during the catalytic process.

Generally the catalytic activity of palladium phosphinite complexes **2** and **3**, as represented by the yield of ester, is high, though slightly lower than that of complex **5**, the final product of their

Table 4 Methoxycarbonylation of iodobenzene catalyzed by palladium phosphinite (**1–5** and **8**) and phosphonite (**6**, **7**) complexes

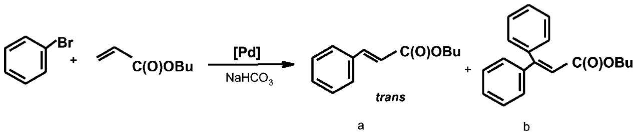
Catalyst	Yield of ester (%)	Catalyst	Yield of ester (%)
1	81	**5**	92
2	66	**6**	100
3	70	**7**	100
4	95	**8**	46

Reaction conditions: [Pd] = 1.41 × 10^{-5} mol; [PhI] = 9.4 ×10^{-3} mol; [[^{n}Bu$_4$N]Cl] : [PhI] = 1; [NEt$_3$] : [PhI] = 2.2; 90 °C, 3 h

hydrolysis. One can conclude that hydrolysis is not very efficient under carbonylation reaction conditions, because of the presence of methanol as well as some water in the hygroscopic ammonium salt. Similar yields of ester obtained in reactions catalyzed by **4** and **5** indicate probable total hydrolysis of **4** during the reaction.

The high catalytic activity of both phosphonate complexes, **6** and **7**, suggests that they may be perfect methoxycarbonylation catalysts. Their additional advantage is high resistance to pH changes, as was demonstrated in reactions with NEt$_3$ and HCl.

Heck coupling of bromobenzene with butyl acrylate catalyzed by complexes 1–8. Heck reactions of bromobenzene with n-butyl acrylate were performed at 130 °C with [^{n}Bu$_4$N]Br as co-catalyst. The application of a 2.3-fold excess of PhBr *versus* n-butyl acrylate facilitated the formation of not only a *trans*-monoarylated (a) but also a diarylated product (b) (Scheme 8).



Scheme 8 Heck cross-coupling.

The activities of the catalysts under study were compared on the basis of the reaction product ratio as well as the stability of the catalytic systems in repetitive experiments (runs 1–3). Higher-activity catalysts produced more of the diarylated product and were successfully recycled several times without a significant lowering of the reaction yield (Table 5).

The results presented in Table 5 indicate very good catalytic performance with all the catalysts studied. In all reactions, even after catalyst recycling, the conversion of butyl acrylate was 95–100%. In most cases the diarylated product was formed with reasonable yield even in the third run, confirming the high activity and stability of the systems. Comparison of results obtained with phosphinite complexes **2–4** and with the dimer **5** leads to the conclusion that the dimer is more active and hydrolysis of complexes **2–4** is a relatively slow process under the Heck reaction conditions, like in the case of methoxycarbonylation. Complex **8**, which presented the lowest productivity in methoxycarbonylation, appeared to be quite a good catalyst in the Heck coupling. Both phosphonate complexes, **6** and **7**, also gave very good results, **7** being slightly better than **6** if the yield of the diarylated product is considered.

Table 5 The yield of Heck coupling reactions catalyzed by palladium phosphinite (**1–5**, **8**) and phosphonite complexes (**6**, **7**) (Scheme 8)

Catalyst	Run 1		Run 2		Run 3	
Product	Mono (a)	Di (b)	Mono (a)	Di (b)	Mono (a)	Di (b)
1	64	36	68	27	63	37
2	58	42	86	10	39	61
3	75	25	86	11	91	5
4	50	50	63	37	20	3
5	75	25	29	71	40	60
6	45	55	80	20	81	7
7	62	38	65	35	76	24
8	41	59	68	30	61	0

Reaction conditions: [Pd] = 1.41 × 10^{-5} mol; [PhBr] = 9.4 × 10^{-3} mol; [CH_2=CHC(O)OBu] = 4.36 × 10^{-3} mol; [[^{n}Bu$_4$N]Br] = 2.3 × 10^{-3} mol; [NaHCO$_3$] = 4.4 × 10^{-3} mol; 140 °C, 4 h.

Conclusions

The reported results demonstrate that phosphonite and phosphonato palladium complexes are ideal catalysts of reactions of aryl halides, representing high activity, stability and recyclability.

Phosphonite palladium complexes of formula PdCl$_2$(PPh$_2$(OR))$_2$, where R = C$_6$F$_5$ **2**, ^{t}Bu **3**, or O-menthyl **4**, undergo hydrolysis in the presence of water and form the dimeric complex [μ-ClPd(PPh$_2$OH)(PPh$_2$O)]$_2$ **5**. The catalytic activity of **5** in methoxycarbonylation and in the Heck cross-coupling is higher than that of complexes **2–4**, which means that hydrolysis of phosphinite complexes improves the catalytic systems.

The phosphinite complex PdCl$_2$(PPh$_2$(OBu))$_2$ **1**, which is not hydrolyzed in the presence of water, exhibited catalytic properties similar to those of **5**.

Deprotonation of **5** by NEt$_3$ led to the polymeric species **8**, containing P(O)Ph$_2^-$ moieties. The reaction is reversible, and the addition of HCl led to the recovery of **5**. These reactions are very important in catalytic systems in which a base is always present and HX is formed as a side product during methoxycarbonylation as well as during the Heck reaction.

The phosphonato complexes, [μ-ClPd(P(OPh)$_2$OH)(P(OPh)$_2$O)]$_2$ **6** and [Pd[P(O)(OPh)$_2$]$_2$]$_n$ **7**, represent a new class of highly active and stable catalysts of both methoxycarbonylation and Heck coupling reactions. The slightly soluble polymeric species **7** can be easily transformed to the soluble dimer **6** in acidic conditions, as was demonstrated by its reaction with HCl. This transformation, very probable also under catalytic reaction conditions, can stabilize palladium in its active form.

Experimental

Syntheses

Palladium complexes **1**, **2** and**3** were obtained according to the method described in ref. 11.

PPh$_2$(O-menthyl). 10 mmol of L-menthol was dissolved in THF under an atmosphere of N$_2$ and then 10 mmol of n-butyllithium in hexane was added dropwise with efficient cooling. The reaction mixture was vigorously stirred for 1 h, cooled to −78 °C and then 10 mM of the phosphine PPh$_2$Cl dissolved in a few cm^3 of THF was added dropwise. The cooling bath was removed and the mixture was stirred for 24 h. After that time THF was removed and the viscous oil obtained was dissolved in *ca.* 20 cm^3 of diethyl ether and filtered through a pad of Celite to remove LiCl. The ether was next removed under vacuum or the phosphinite was used for further syntheses in ether solution. MS: 340 (M^+), 201 ($OPPh_2$), 183 (PPh_2), 155 (menthyl). ^{31}P NMR ($CDCl_3$): 107.3 ppm.

$PdCl_2[PPh_2(O\text{-menthyl})]_2$, 4. To 0.11 g of $PdCl_2$(cod) in 2 cm^3 of CH_2Cl_2 0.5 cm^3 of diethyl ether containing 1 mmol of PPh_2(O-menthyl) was added. The yellow solution was stirred for 15 min and evaporated to dryness. The residue was washed with hexane giving a pale yellow precipitate. Yield: 76% Anal. Calc. for $PdC_{44}H_{58}O_2P_2Cl_2$: C, 61.6; H, 3.38. Found: C, 61.1; H, 3.5%. ^{1}H NMR ($CDCl_3$): 0.4 d (J(H–H) 7 Hz), 0.81 d (J(H–H) 7 Hz), 0.87 d (J(H–H) 7 Hz), 1.5 m, 2.53 m, 3.27 m, 5.26 m, 7.06 m, 7.92 m; ^{31}P NMR ($CDCl_3$): 100.2 ppm; UV-Vis ($CHCl_3$): 264, 340 nm; IR/KBr (cm^{-1}): 2900vs, 1420s, 1100s, 1000vs, 680s, 530s, 500s; IR/Nujol (cm^{-1}): 316.

$[\mu\text{-ClPd}(PPh_2OH)(PPh_2O)]_2$, 5. To 0.066 g $PdCl_2$(cod) 0.2 cm^3 of PPh_2Cl in 2 cm^3 of benzene was added and the resultant mixture was stirred for 2 h. Next H_2O (0.05 cm^3) was added and after 5 min 2 cm^3 of EtOH. Stirring was continued for 1 h and the resultant white precipitate was filtered off, washed with ethyl ether and dried. Yield: 0.17 g. Anal. Calc. For $Pd_2Cl_2C_{48}H_{42}O_4P_4$: C, 52.89; H, 3.70 Found: C, 52.64; H, 3.50%. IR/KBr (cm^{-1}): 1480vs, 1100vs, 1015m, 730m, 710m, 680vs, 500m; IR/Nujol (cm^{-1}): 333.3, 275.0 (ν(Pd–Cl)); UV-Vis ($CHCl_3$): 350 nm; ^{1}H NMR($CDCl_3$): 7.15m (Ph), 10.0 br (OH) ppm. ^{31}P NMR($CDCl_3$): 76.6 ppm (at 500 MHz with methylenediphosphonic acid as external standard), 78.0 ppm (at 300 MHz with 85% H_3PO_4 as external standard).

$[\mu\text{-ClPd}(P(OPh)_2OH)(P(OPh)_2O)]_2$, 6. To 0.07 g of $PdCl_2$(cod) in 1 cm^3 of benzene 0.12 cm^3 of $P(OH)(OPh)_2$ was added and a white precipitate formed immediately. The mixture was stirred for 1 h and after that time the product was filtered off, washed with diethyl ether and dried *in vacuo*. Yield: 0.09 g. Anal. Calc. For $Pd_2Cl_2C_{48}H_{42}O_{12}P_4$: C, 47.4; H, 3.3 Found: C, 47.1; H, 3.19%. IR/KBr (cm^{-1}): 1600s, 1480vs, 1200vs, 900vs, 750m, 700m, 500m; IR/Nujol (cm^{-1}): 381.7, 338.0 (ν(Pd–Cl)); ^{1}H NMR($CDCl_3$): 7.15m (Ph), 10.0 br (OH) ppm; ^{31}P NMR($CDCl_3$: 65.5 ppm.

$[Pd[P(O)(OPh)_2]_2]_n$, 7. To 0.22 g of $Pd(OAc)_2$ in 2 cm^3 of benzene 0.4 cm^3 of $P(OH)(OPh)_2$ was added and the resultant mixture was stirred at ambient temperature. After a few minutes the solution became homogeneous and colourless, then a white precipitate started to form. Stirring was continued for 2 h and next diethyl ether was added to complete precipitation of product which was filtered off and dried *in vacuo*. Yield: 0.38 g. IR/KBr (cm^{-1}): 1600s, 1490vs, 1200vs, 1100vs, 920vs, 760m, 700m, 500m; IR/Nujol(cm^{-1}): 3400 (ν(OH)); ^{31}P NMR ($CDCl_3$, measured *in situ*): 86.8 ppm.

$[Pd[P(O)Ph_2)]_2]_n$, 8. To a solution of complex **5** (0.05 g) in 1 cm^3 of $CHCl_3$ triethylamine (0.05 cm^3) was added dropwise. After a few minutes a pale yellow precipitate was formed, which was filtered off, washed with $CHCl_3$ and dried under vacuum. Yield; 0.038 g. IR/KBr (cm^{-1}): 1437s, 1108s, 1022vs, 742m, 713m, 690s, 535s.

Measurements

^{1}H, and ^{31}P NMR spectra were recorded on Bruker 300 and Bruker 500 spectrometers. For ^{31}P NMR at 300 MHz 85% H_3PO_4 was used as an external standard and at 500 MHz methylenediphosphonic acid was used as an external standard.

FTIR spectra were measured on Nicolet Impact 400 spectrometer.

GC-MS an GC analyses were made on a Hewlett Packard 8452A instrument.

Catalytic reactions

The Heck reactions were carried out in a Schlenk tube with magnetic stirring. The catalyst (1.41 × 10^{-5} mol) was weighed in a small Teflon vessel, $[^nBu_4N]Br$ (2.3 × 10^{-3} mol) and $NaHCO_3$ (4.4 × 10^{-3} mol) were introduced to the Schlenk tube which was next evacuated and filled with N_2. Reagents: 1.89 × 10^{-3} mol of butyl acrylate, 4.36 × 10^{-3} mol of bromobenzene and 7.15 × 10^{-4} mol of mesitylene (internal standard) were introduced under an N_2 atmosphere. Next the Schlenk tube was sealed with a rubber tap and introduced into an oil bath pre-heated to 140 °C for the reaction time 4 h. After that time the Schlenk tube was cooled and any organic products were separated by extraction with diethyl ether (3 times with 10 cm^3) and GC-FID analyzed (Hewlett Packard 8452A). The products were identified by GC-MS (Hewlett Packard 8452A). ^{1}H NMR spectroscopy was used as a complementary method of product identification as well as determination of the reaction yield. Samples for ^{1}H NMR measurements were prepared in $CDCl_3$ after vacuum removal of diethyl ether from the extract.

For recycling experiments the solid residue obtained after the extraction of the liquid products was dried in vacuum, next the liquid reagents and $NaHCO_3$ in the amounts given above were added under a N_2 atmosphere.

The methoxycarbonylation reactions were carried out in a 130 cm^3 thermostated steel autoclave with magnetic stirring. Reagents: PhI (9.4 × 10^{-3} mol), NEt_3 (2.15 × 10^{-2} mol), methanol (2.5 × 10^{-2} mol), mesitylene-internal standard (4.6 × 10^{-3} mol), and palladium catalyst (1.41 × 10^{-5} mol), were introduced into the autoclave under an N_2 atmosphere. Next, the N_2 atmosphere was replaced by CO (5 atm). The reaction was carried out at 90 °C for 3 h. Afterwards, the autoclave was cooled and any organic products were separated by extraction with diethyl ether (3 times with 3 cm^3) and GC-FID analyzed (Hewlett Packard 8452A) or condensed under vacuum to remove diethyl ether and analyzed using ^{1}H NMR spectroscopy (Bruker 500 MHz) after $CDCl_3$ addition.

X-Ray crystallography

A suitable crystal was glued on top of a glass fiber and transferred into the cold nitrogen stream on a Kuma KM4CCD κ-axis diffractometer (graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å). The crystal was positioned at 65 mm from the CCD camera. 612 frames were measured at 0.75° intervals with a counting time of 20 s. Accurate cell parameters were determined and refined by least-squares fit of 4800 of the strongest reflections. Data were corrected for Lorentz and polarization effects. Analytical absorption correction was also applied. Data reduction and analysis were carried out with the Oxford Diffraction (Poland) programs. The structure was solved by the heavy method (program SHELXS97[31]) and refined by the full-matrix least-squares method on all F^2 data using the SHELXL97 programs.[32] Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included from the geometry of the molecules and the ΔF map but were not refined (except the H1 atom). Neutral atom scattering factors were taken from Cromer and Waber.[33] Final refinement details are: Chemical formula: $C_{60}H_{54}O_4Cl_2P_4Pd_2$, formula weight ($M$) 1246.65; crystal system: monoclinic; unit-cell dimentions (Å, °): $a = 8.6925(6)$; $b = 16.1096(7)$; $c = 20.1450(10)$; $\beta = 102.338(5)$; $V/\text{Å}^3 = 2755.8(3)$; $T/\text{K} = 100(2)$; space group: $P2_1/c$; $Z = 2$; μ (mm^{-1}) = 0.912; reflections measured: 17881; independent reflections: 5996 (0.0266); Final R_1/wR_2 indices ($I > 2\sigma_I$): 0.0246/0.0559.

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For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512835h

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