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Synthesis of benzylpalladium complexes through C–O bond cleavage of benzylic carboxylates: Development of a novel palladium-catalyzed benzylation of olefins

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Abstract

Benzylic carboxylates were found to react with Pd(0) complexes bearing tertiary phosphines to give benzylpalladium(II) carboxylate complexes with cleavage of the benzyl-oxygen bond. The benzylpalladium complexes having the trifluoroacetato ligand react with olefins such as ethyl acrylate to give olefin benzylation products. On the basis of these studies a novel palladium-catalyzed benzylation of olefins was developed without using organic halides as the starting materials. The method has another advantage of requiring no base as in the conventional Mizoroki–Heck process using organic halides. The catalytic cycle is proposed to be constituted of elementary processes of (a) oxidative addition of a benzyl carboxylate with C–O bond cleavage to a Pd(0) complex to give a benzylpalladium carboxylate, (b) olefin insertion into the benzylpalladium bond to give an alkylpalladium complex, and (c) β-H abstraction to liberate the benzylated olefin.

Keywords: Benzylation; Palladium catalyst; Benzyl-O bond cleavage, Olefin synthesis; Benzylpalladium carboxylate

1. Introduction

Among various palladium-catalyzed processes to perform the C–C bond formation in organic synthesis [1], the palladium-catalyzed olefin arylation (or vinylation), called Mizoroki–Heck processes have been extensively utilized as fundamental tools in organic synthesis [2]. Palladium-catalyzed cross-coupling processes of aryl halides with other organometallic reagents also rank among the most utilized processes. Mechanistically, these two types of processes involve cleavage of the carbon–halogen bond in organic halides on their interaction with electron-rich Pd(0) complexes to generate reactive organopalladium(II) halide species by oxidative addition. In the olefin arylation the subsequent insertion process to give palladium alkyls followed by β-H abstraction yields arylated olefins, whereas coupling of the arylpalladium complexes with other organometallic compounds by transmetallation followed by reductive elimination produces the cross-coupling products [3].

However, the both processes entail intrinsic problems of using organic halides as substrates for preparation of products that contain no halogen and addition of a base is required for performing the Mizoroki–Heck processes with production of salt wastes. Thus finding a methodology without using halides to be removed with a base is desirable for making the process more atom efficient and environmentally benign.

An approach for finding a halogen-free catalytic process is to utilize an organic compound that is susceptible to cleavage of the carbon–hydrogen or carbon–heteroatom bond for producing organopalladium complexes. We have been interested in the elementary processes where a carbon–oxygen bond in an oxygen-containing organic compound is cleaved on interaction with a low valent transition metal complex and have found several new palladium-catalyzed

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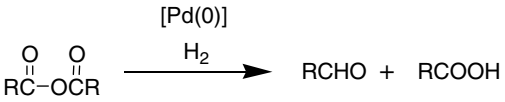
processes using the cleavage of the C–O bond in carboxylic esters and carboxylic anhydrides [4–8].

In previous studies we have found that carboxylic anhydrides readily undergo the oxidative addition on interaction with Pd(0) complexes to afford acylpalladium carboxylates with cleavage of the acyl-O bond [5]. Aryl esters such as aryl trifluoroacetates also undergo the oxidative addition involving the acyl-O cleavage to give acylpalladium aryloxide complexes (Scheme 1) [6].

Utilizing the reactivity of the acylpalladium complexes with hydrogen to release aldehydes and carboxylic acids, we could develop a palladium-catalyzed process to synthesize aldehydes from carboxylic anhydrides without using organic halides (Eq. (1))



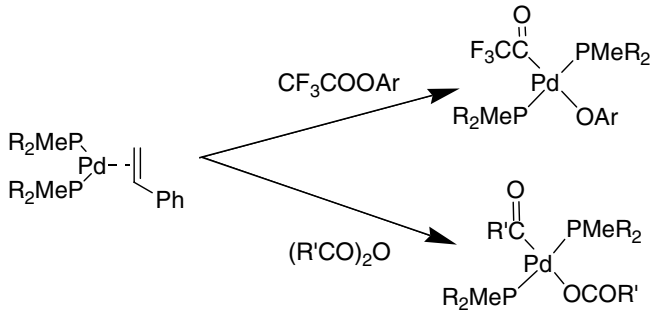
(1)

As another application of the concept of the C–O bond cleavage to give acylpalladium complexes, we have developed a new process to prepare ketones and perfluoroketones by combination of the C–O bond cleavage in carboxylic anhydride with transmetallation with arylboronic acids as arylation reagents, providing with further examples of utility of the process involving the Pd-promoted C–O bond cleavage [9,10].

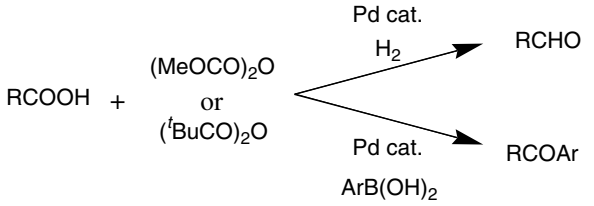
The concept of the C–O bond cleavage combined with other elementary processes was further expanded so that we can use the carboxylic acids themselves without using the preformed carboxylic anhydrides or carboxylic esters by using additives such as less reactive carboxylic anhydride or dicarbonates (Scheme 2) [11,12].

Gooßen also reported similar catalytic processes to produce aldehydes [13] and ketones [14] on the basis of a similar concept under somewhat different experimental conditions. Further example of ketone synthesis utilizing cleavage of the acyl-O bond cleavage in pyridyl carboxylate combined with the transmetallation using organoboronic acids has been also reported [15].

As another type of palladium-catalyzed processes involving the C–O bond cleavage, palladium-catalyzed allylation of nucleophiles using allylic carboxylates and



Scheme 1. Cleavage of C–O bond in aryl trifluoroacetates and carboxylic anhydrides.



Scheme 2. Synthesis of aldehydes and ketones from carboxylic acids.

carbonates (Tsuji-Trost Process) have been extensively used in organic synthesis [16]. The catalytic process can be accounted for by combination of the C–O bond cleavage of the allyl carboxylate with Pd(0) complex giving an η^3-allylpalladium complex with the subsequent nucleophilic attack on the allyl ligand. Another type of application involving the cleavage of the allyl-oxygen bond in allylic carboxylate is the palladium-catalyzed reduction of allylic formate to alkenes [17].

In contrast to these methods, combination of the allyl-O bond cleaving process with olefin insertion has been mostly limited to intramolecular synthesis of cyclic compounds, presumably due to the difficulty of olefin insertion into the η^3-allylpalladium intermediate [18,19]. Recent development is the palladium-catalyzed cleavage of allylic alcohols combined with insertion of olefins to give dienes [20]. Limited examples for achieving the olefin allylation with benzyl chloride are known [21].

An approach for accomplishing the palladium-catalyzed halide-free olefin arylation process has been developed by de Vries and coworkers [22]. They utilized the concept of the C–O bond cleavage of carboxylic anhydrides on interaction with a Pd(0) complex and combined it with an olefin insertion process. The process proceeds through oxidative addition of a carboxylic anhydride to give an aroylpalladium carboxylate followed by decarbonylation to provide an arylpalladium carboxylate, into which olefin insertion takes place. Application of a related idea to Rh-catalyzed coupling of an aroyl group in carboxylic anhydride with olefin insertion and hydrogenation was developed by Miura and coworkers [23].

Based on a related concept, Gooßen and coworkers developed a new type of olefination of aryl carboxylate involving the oxidative addition with the C–O bond cleavage, followed by decarbonylation and the olefin insertion process. [24], They have further expanded the method to direct conversion of carboxylic acids and olefins into olefin arylation products in the presence of a dicarbonate [25–27].

In contrast to the extensive application of allylic carboxylates, benzyl esters having allylic nature have attracted much less attention as the starting material. Fiaud and Legros reported the benzylic substitution of naphthylmethyl carboxylate [28], and Kuwano recently found that benzyl carboxylates undergo the nucleophilic substitution at the benzylic group in the presence of palladium catalysts with nucleophiles such as malonates, amines, and thiols [29] as well as sulfinates [30]. Further application of the palladium-catalyzed C–O bond cleavage in benzylic alcohols

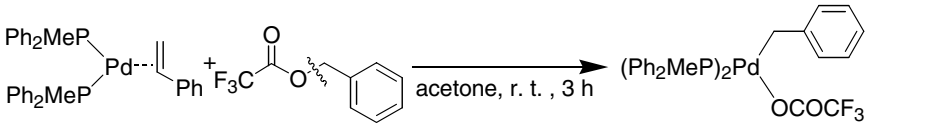
to cross-coupling reactions to synthesize ketones and diarylmethanes were also developed [31]. In another type of application of benzylic alcohols, production of ethers, amines and thioethers has been reported [32], while a different mechanism from the present examples is proposed.

The application of benzyl halides to the Mizoroki–Heck olefin arylation has so far received less attention but palladium-catalyzed benzylation of olefins with benzylic chlorides has been reported [33].

In the first part of the present paper we first examined the reactions of benzyl carboxylates with Pd(0) complexes to establish the oxidative addition products of benzyl carboxylates. The reactivity of the benzylpalladium complexes with olefins was then examined to see if olefin insertion into the benzylpalladium bond takes place.

In the second part of the paper, we examine the application of the information thus obtained to development of the catalytic olefin benzylation process with benzyl carboxylates. On the basis of the fundamental properties of benzylpalladium complexes with olefins we propose a reasonable catalytic cycle for the benzylation of olefins. The present paper also provides experimental data concerning the results we reported briefly in the previous communication [34].

On the other hand, the reaction of the $PMePh_2$-coordinated Pd(0) complex, [Pd(styrene)($PMePh_2$)$_2$] (**2b**) with more electronegative benzyl trifluoroacetate took place smoothly at room temperature to give **3c** as pale yellow crystals (Eq. (2)). In our previous study of the synthesis of **3c** and other related complexes [38], we observed the formation of two isomers of the benzylpalladium complexes in various solvents as suggested by NMR studies. We assigned the *trans* and "*cis*" configurations to these isomers observed in solutions, where the *trans* isomer dominated



2b

trans-**3c** (major) + *"cis*-**3c***"* (minor)

93 % (2)

2. Results

2.1. Synthesis and characterization of benzyl(carboxylato)-palladium complexes

The coordinatively unsaturated Pd(0) complex, [Pd(styrene)(PMe_3)$_2$] (**2a**) [35], prepared in situ by thermolysis of [$PdEt_2$(PMe_3)$_2$] (**1a**) [36] in the presence of styrene, was found to react readily with benzyl carboxylates with the benzyl-O bond cleavage to give benzyl(carboxylato)palladium complexes **3a** and **3b** as shown in Scheme 3.

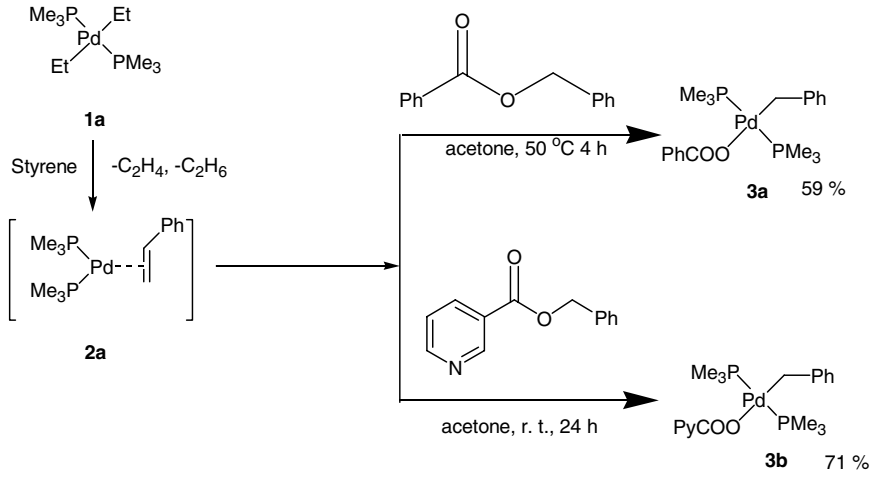
The PMe_3-coordinated *trans*-benzyl(benzoato)palladium complex **3a** and *trans*-benzyl(nicotinato)palladium complex **3b** were characterized by elemental analysis and ^{1}H, ^{13}C, and ^{31}P NMR spectra. The *trans* configuration of **3a** and **3b** was supported by observation of the methyl protons in the *trans*-situated PMe_3 ligands as virtual triplets and of the benzyl CH_2 protons as a triplet due to coupling with the two mutually *trans*-situated PMe_3 ligands. The ^{31}P NMR spectra of these complexes showed a singlet, respectively, in agreement with the trans geometry [37,6].

The ^{31}P{^{1}H}NMR spectra of the minor isomer showed two doublets and the ^{1}H NMR of the benzylic protons exhibited a doublet. The spectroscopic patterns were compatible with the configuration of the complex having the two $PMePh_2$ ligands coordinated with the center metal in mutually adjacent positions, thus we ascribed the minor species to the "*cis*" isomer and studied the equilibrium between the *trans* isomer and the other isomer presumed to have the *cis* configuration.

However, we later realized that the minor isomer to which we assigned the "*cis*" structure may have an ionic structure with the two $PMePh_2$ ligands in mutually adjacent positions and a trifluoroacetato anion, as will be discussed later.

We first determined the molecular structure of the crystals deposited from a THF solution by single crystal X-ray analysis and found that the η^1-benzylpalladium complex having the PPh_2Me ligands, **3c**, has the square planar configuration with the *trans* geometry as shown in Fig. 1 [39,40].

Examination of the determined molecular structure of *trans*-**3c** confirms the square planar *trans* configuration having the η^1-benzyl ligand at the site *trans* to the trifluoroacetato ligand. Further inspection of the results of the molecular structure shows that the two mutually *trans*-situated $PMePh_2$ ligands are slightly distorted away from the benzyl ligand in the square planar geometry and are bent toward the CF_3COO^- ligand with the P–Pd–P angle of 170.18 degree. The CF_3COO–Pd bond is somewhat lengthened to 2.150(4) Å from the usually observed Pd–O distances in the phosphine-bearing palladium trifluoroacetate complexes ranging from 2.05 to 2.07 Å [37]. The elongation of the palladium–oxygen bond in the trifluoroacetato ligand may reflect the *trans* influence of the benzyl ligand or inclination of the trifluoroacetato ligand to dissociate from the

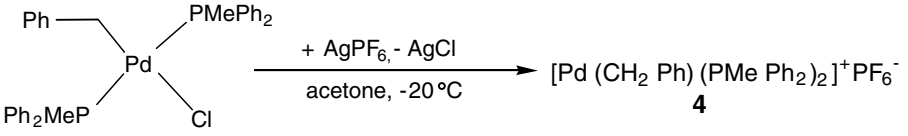


Scheme 3. Oxidative addition of benzyl esters with benzyl C–O bond cleavage.

Pd center, particularly in polar solvent. The phenyl ring in the benzylpalladium complex is oriented to be perpendicular to the molecular plane. The Pd-benzylic carbon bond distance of 2.070(6) Å is similar to the value of 2.08 Å in *trans*-[Pd($CH_2C_6H_4$-*p*-Br)Br(PMe_3)$_2$] [37].

The NMR spectra of the major isomer observed in solutions are consistent with the *trans* configuration.

Since isolation of the minor isomer was not feasible, we prepared an ionic benzylpalladium complex having the PF_6 anion, [($PhCH_2$)($PMePh_2$)$_2$Pd]PF_6 (**4**), by treatment of the neutral *trans*-benzylpalladium chloride complex with $AgPF_6$ in acetone solution at −20 °C (Eq. (3)) and compared its NMR spectra with those of the minor isomer

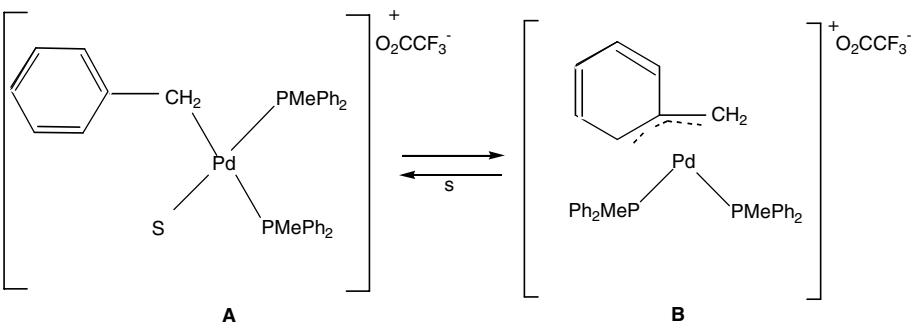


(3)

The ^{1}H NMR peaks of the methylene protons in the benzyl group in complex **4** showed a broad doublet. On the other hand, the $^{13}C\{^1H\}$ NMR spectrum of **4** showed the coupling of the benzylic carbon with the two $PMePh_2$ ligands as a doublet of doublets (dd, $J = 6.41$ and 38.95 Hz). The $^{31}P\{^1H\}$ NMR showed the two doublets, consistent with the structure having two adjacent $PMePh_2$ ligands. The spectroscopic patterns of the ionic complex **4** were thus revealed to be quite similar to those of the minor isomer of **3c**.

We have previously prepared an ionic benzylpalladium complex having two PPh_3 ligands and PF_6^- anion by decarbonylation of a phenylacetylpalladium complex having two PPh_3 ligands [6] and by removing chloride ligand in *trans*-$PhCH_2PdCl(PMe_3)_2$ complex with $AgPF_4$ in acetone [6]. The benzylpalladium complexes having two tertiary phosphine ligands obtained in the present study showed similar spectroscopic patterns consistent with ionic structure having two mutually adjacent PR_3 ligands and a PF_6^- counter ion.

However, for the ionic benzylpalladium complexes having two *cis* PR_3 ligands there remains the possibility of existence of two isomers, a solvent coordinated η^1-benzyl isomer **A** and η^3-benzyl isomer **B**, as shown in Eq. (4). These η^1 and η^3 isomers may be reversibly convertible and there may be an equilibrium between the two isomers in solutions



(4)

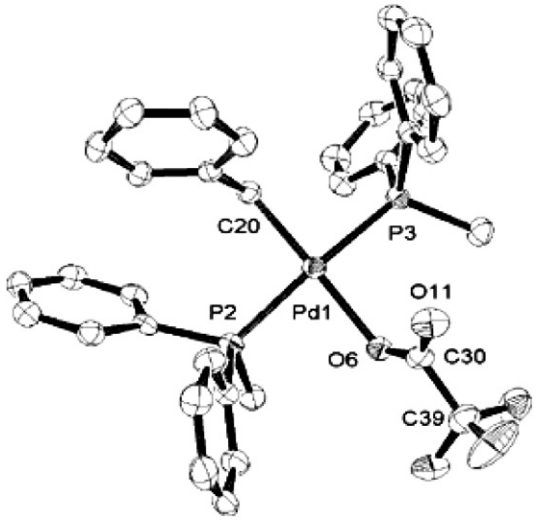


Fig. 1. Perspective view of the *trans*-[benzyltrifluoroacetatobis(methyldiphenylphosphine)Pd(II) complex, *trans*-**3c**.

Table 1
Selected bond lengths (Å) and angles (°) for complex **3c**

P2–Pd1	2.316(2)	P3–Pd1	2.307(2)
O6–Pd1	2.150(4)	C20–Pd1	2.070(6)
P2–Pd1–O6	84.1(1)	P2–Pd1–P3	170.18(6)
P3–Pd1–O6	93.7(1)	P3–Pd1–C20	88.0(2)
C20–Pd1–P2	94.1(2)	C20–Pd1–O6	178.0(2)

Table 2
Equilibrium ratio of neutral *trans*-η^1- and "*cis*"-ionic benzylpalladium isomers in chloroform and DMF solutions

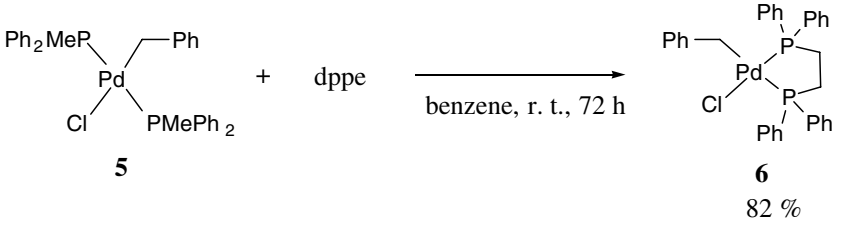
neutral *trans*-η^1-complex ⇄ *trans*: "*cis*"-complex[a] (6)

Solvent	Temperature (°C)	*trans*: "*cis*"-Complex
$CDCl_3$	−20	4.6:1
	−10	4.6:1
	0	4.6:1
	10	4.6:1
	20	4.6:1
DMF-d_7	−20	1: 1.02
	−10	1: 1.09
	0	1: 1.23
	10	1: 1.39
	20	1: 1.47

[a] Determined by ^{1}H NMR.

Distinction of the two isomers by NMR is difficult and unequivocal assignment of the structure was not feasible. Furthermore, an interconversion process between the solvent-coordinated η^1-benzyl isomer **A** and η^3-benzyl isomer **B** may be operative. Thus we tentatively assign the *cis*-like structure for the ionic benzylpalladium complex without distinction between **A** and **B**.

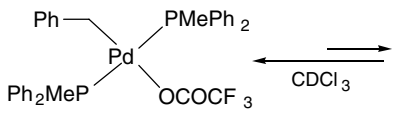
For gaining further information regarding the ^{1}H, ^{13}C, and ^{31}P coupling patterns of the benzylpalladium isomer of **3c**, we prepared a neutral η^1-benzylpalladium complex **6** having a ditertiary phosphine ligand, dppe from **5**, as shown in the following equation:



(5)

and the ^{31}P{^{1}H} NMR showed two doublets arising from the two phosphine ligands in agreement with the structure of **6** in Eq. (5). The ^{1}H NMR pattern of the benzylic CH_2 protons in **6** observed as the doublet of doublets differs from that of the benzylpalladium **3c** observed as a doublet.

The observation of the minor isomer of **3c** in solutions may now be interpreted by assuming the partial dissociation of the trifluoroacetato ligand in solutions from the neutral *trans*-η^1-benzyl isomer to give the cationic, solvent-coordinated "*cis*"-η^1-benzylpalladium complex (**A**) or cationic "*cis*"-η^3-benzylpalladium complex (**B**) (see Eq. (4)) as shown below (see Table 1)



ionic *cis*"-[(η^1–benzyl)(s)Pd($PMePh_2$)$_2$]$^+$$OCOCF_3^-$ (**A**)

or

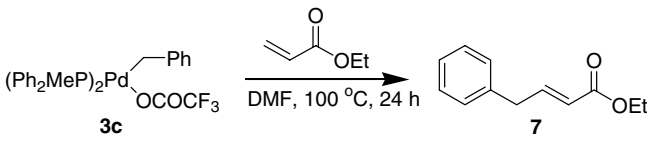
ionic "*cis*"-[η^3–(benzyl)Pd($PMePh_2$)$_2$]$^+$$OCOCF_3^-$ (**B**)

(6)

neutral *trans*-η^1–benzyl form

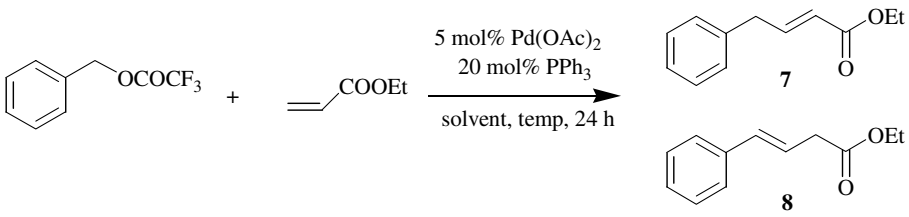
The benzylpalladium complex **3c** was found to exist in the *trans* to "*cis*" ratio of 4.6:1 in $CDCl_3$ solution with little change in the isomer ratio between −20 °C and 20 °C. On the other hand, the NMR spectrum of complex **3c** observed in DMF-d_7 of larger polarity showed the increase of the ionic "*cis*"-benzylpalladium isomer, from 1:1.0 at −20 °C to 1:1.5 at 20 °C as shown in Table 2. On raising the temperature the signals arising from the *trans* isomer in the η^1-benzyl form and from the ionic "*cis*"-benzyl form showed broadening. The change of the ratio of the two forms depending on temperature was reversible and lowering the temperature restored the original spectroscopic pattern.

Determination of the equilibria in Eq. (6) at various temperatures and performing the Eyring plot of the K values obtained at various temperatures led to the ΔH value of 6.0 kJ/mol and ΔS value of 0.02 kJ/mol K for the equilibrium.



(7)

The higher reactivity of the benzylpalladium trifluoroacetate complex **3c** in polar solvents that favor the dissociation of the CF_3COO^- anion, suggested enhancement of the reactivity of the benzyl complex by partial dissociation of the anionic ligand in a polar solvent. In fact the ionic complex, (η^3-benzyl)bis(methyldiphenylphosphine)palladium hexafluorophosphate, **4** smoothly reacted with ethyl acrylate in $CHCl_3$ at 80 °C to give ethyl (*E*)-4-phenyl-2-butenoate **7** and its isomer (*E*)-4-phenyl-3-butenoate **8** in a ratio of 62:13 with the combined yield of 75% at 80 °C.



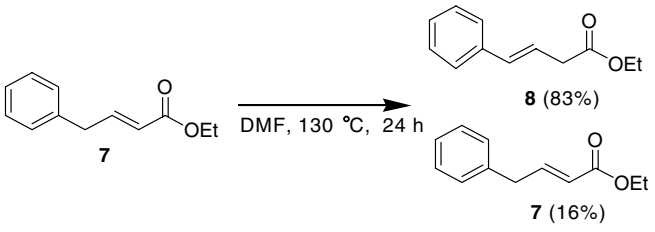
(8)

These results suggest that the benzylpalladium complex tends to dissociate the trifluoroacetato ligand to a greater degree in solvents of larger polarity, and the dissociation of the CF_3COO^- anion in a polar solvent is somewhat favored at a higher temperature. The dissociation of the anionic ligand in solution may have implications to the enhancement of the reactivity of the benzylpalladium complex with olefins in polar solvents as we discuss later.

2.2. Reactions of benzyl(carboxylato)palladium complexes with ethyl acrylate

Having established the structures of the benzylpalladium complexes derived by oxidative addition of benzyl carboxylate with the Pd(0) complex and gained some information on their behavior in solutions, we next examined the reactivity of the benzylpalladium complexes toward olefins. The *trans*-benzyl(benzoato)palladium(II) complex **3a** and *trans*-benzyl(nicotinato)palladium(II) complex **3b** did not react with ethyl acrylate neither in $CDCl_3$, nor in DMF-d_7 under refluxing conditions of each solution and deposited only black precipitate. On the other hand, the benzyl(trifluoroacetato)palladium complex **3c** reacted with ethyl acrylate in DMF-d_7 at the elevated temperature of 100 °C and yielded ethyl (*E*)-4-phenyl-2-butenoate **7** in 25% yield, whereas no reaction proceeded in $CDCl_3$ (Eq. (7))

The isomer **8** may have been produced by thermal isomerization of **7**, as was independently verified by heating the DMF solution of **7** at 130 °C (Eq. (9))



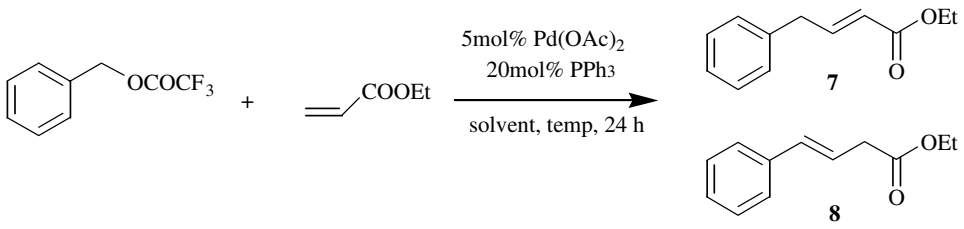
(9)

The occurrence of the olefin insertion into the benzylpalladium bond in **4** followed by β-H elimination to liberate the benzylated olefin indicated the feasibility of application of the benzyl-O bond cleavage of benzyl carboxylates to catalytic olefin benzylation processes in the presence of a palladium catalyst. In fact, we could realize the palladium-catalyzed olefin benzylation processes with benzyl trifluoroacetates *without using organic halides in the absence of a base.*

2.3. Catalytic olefin benzylation with benzyl trifluoroacetates

No catalytic benzylation of ethyl acrylate was observed in the reaction of benzyl benzoate with various catalysts such as $Pd(OAc)_2$, $Pd(OAc)_2 + PPh_3$, $Pd(OAc)_2 + 2PBu_3$, $Pd(PCy_3)_2$, $Pd(dba)_2 + PPh_3$, $PdCl_2$, $PdCl_2$ + isoquinoline,

Table 3
Effects of solvents and reaction temperatures on palladium-catalyzed benzylation of ethyl acrylate using benzyl trifluoroacetate



Run	Solvent	Temperature (°C)	Yield (%)[a] (**7**:**8** ratio)
1	THF	Reflux	N.R.
2	Toluene	80	N.R.
3	NMP	80	Trace
4	DMSO	80	24
5	DMF	80	31
6	DMF	100	61 (20:1)[b]
7	DMF	120	68 (1:1)
8	DMF	140	46 (1:5)

[a] Isolated yield.
[b] Ratio of **7**–**8** was determined by ^{1}H NMR.

$PdCl_2 + LiCl$ in polar solvents such as DMF or NMP at elevated temperatures of 100 °C or even at temperatures as high as 160 °C.

Benzyl trifluoroacetate, the more electronegative carboxylate, was found to be more reactive than benzyl benzoate in the catalytic process as observed in the reactions of the isolated benzylpalladium trifluoroacetate with olefins. Table 3 shows the results of reactions of benzyl trifluoroacetate with ethyl acrylate performed in the presence of 5 mol% of $Pd(OAc)_2$ and 20 mol% of PPh_3 in various solvents. The results show that benzyl trifluoroacetate can be catalytically converted into its olefination products under suitable experimental conditions as described below.

2.3.1. Effect of solvent and temperature

In THF, toluene, or NMP (*N*-methylpyrrolidinone) no reaction took place by heating the mixture of benzyl trifluoroacetate and ethyl acrylate at elevated temperatures in the presence of the palladium catalyst. For carrying out the benzylation of ethyl acrylate successfully, employment of polar solvents such as DMSO and DMF was necessary. Dimethyl formamide proved to be most suitable among the solvents examined giving ethyl (*E*)-4-phenyl-2-butenoate **7** in a good yield at 100 °C accompanied by formation of a small amount of its isomerization product, ethyl (*E*)-4-phenyl-3-butenoate, **8**. Carrying out the same reaction in DMF at higher temperature of 120 °C gave a somewhat higher yield of **7** accompanied by formation of a considerable amount of **8**. The reaction at still higher temperature of 140 °C caused decrease in the yield of **7** with extensive isomerization to **8** (Table 3).

2.3.2. Examination of catalytic systems

The catalytic activities of various palladium complexes with tertiary phosphine ligands in the reaction of benzyl trifluoroacetate with ethyl acrylate at 100 °C in DMF was examined and the results are summarized in Table 4.

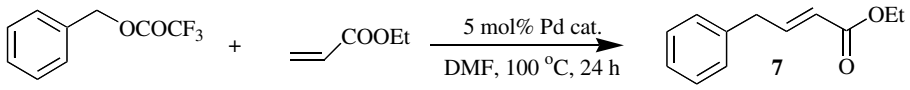
Among various palladium catalysts examined in DMF, combination of $Pd(OAc)_2$ with 4 equiv. of PPh_3 gave the olefin benzylation product **7** in good yields at 100 °C (runs 5 and 6). Employment of ditertiary phosphines such as dppe and dppp was not suitable for the catalysis, and addition of bulky tri-*o*-methylphenylphosphine had an inhibition effect (run 7).

Use of $Pd(OAc)_2$ alone as the catalyst was not effective and addition of a tertiary phosphine such as PPh_3 was necessary to maintain the catalytic activity. Since Pd(0) complexes such as $Pd(PCy_3)_2$ and $Pd(PPh_3)_4$ served as catalysts, it is clear that Pd(0) species plays an important role as catalyst [1]. However, use of the preformed Pd(0) complexes is not necessary and combination of $Pd(OAc)_2$ with tertiary phosphines can be conveniently used as catalyst, probably because $Pd(OAc)_2$ is reduced into Pd(0) in the presence of PPh_3 ligands accompanied by oxidation of PPh_3 to $OPPh_3$ [42,43].

2.3.3. Scope of the catalytic process

We chose the combination of $Pd(OAc)_2$ and 4 equiv. of PPh_3 as a standard catalyst mixture and examined the applicability of the present method to the reactions of various substituted and unsubstituted phenylmethyl trifluoroacetates with various olefins by carrying out the experiments under the standardized procedure. The results summarized in Table 5 demonstrate that the present process is applicable to a broad variety of substrates affording benzylation products of various olefins. Benzyl trifluoroacetates having an electron-withdrawing substituent such as chloride or fluoride at the para position of the phenyl group in the benzyl moiety could be catalytically converted into the corresponding compounds in good yields (Entries

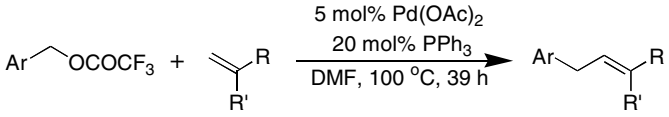
Table 4
Effects of palladium catalysts on benzylation of ethyl acrylate with benzyl trifluoroacetate



Run	Pd cat.		Yield (%)[a]
1	$Pd(OAc)_2$		0
2	$Pd(OAc)_2$	1 PPh_3	34
3	$Pd(OAc)_2$	2 PPh_3	45
4	$Pd(OAc)_2$	3 PPh_3	46
5	$Pd(OAc)_2$	4 PPh_3	61
6[b]	$Pd(OAc)_2$	4PPh_3	75
7	$Pd(OAc)_2$	4 P(*o*-MeC_6H_4)$_3$	0
8	$Pd(OAc)_2$	4 P^{n}Bu$_3$	55
9	$Pd(OAc)_2$	dppe	Trace
10	$Pd(OAc)_2$	dppp	0
11	$Pd(dba)_2$	2 PPh_3	23
12	$Pd(dba)_2$	3 PPh_3	23
13	$Pd(dba)_2$	4 PPh_3	60
14	$Pd(PCy_3)_2$		23
15	$Pd(PPh_3)_4$		49

[a] Isolated yield.
[b] Reaction time was 39.5 h.

Table 5
The palladium-catalyzed benzylation of olefins with benzyl trifluoroacetates



Entry	Ar	R	R′	Yield (%)
1	Ph	COOEt	H	75
2	*p*-$MeOC_6H_4$	COOEt	H	59
3	Ph	*p*-MeC_6H_4	H	65
4	*p*-$MeOC_6H_4$	*p*-MeC_6H_4	H	42
5	*p*-ClC_6H_4	*p*-MeC_6H_4	H	81
6	*p*-FC_6H_4	*p*-MeC_6H_4	H	80
7	Ph	2-pryridine	H	27
8	*p*-$MeOC_6H_4$	Ph	Ph	21
9	*p*-$MeOC_6H_4$	*p*-ClC_6H_4	H	56
10	2,4,6-trimethyphenyl	*p*-MeC_6H_4	H	69
11	3,5,6-trimethoxyphenyl	*p*-MeC_6H_4	H	56

5–6). *p*-Chlorophenylmethyl trifluoroacetate was transformed selectively into corresponding compounds without undergoing the C–Cl bond cleavage.

Substitution at the para position of the benzyl group with the MeO group caused some decrease in the yield of the benzylated olefins as shown in Entries 2, 4, 8, and 9. The process was also applicable to benzylic trifluoroacetates having multiply substituted phenyl groups (Entries 10–11).

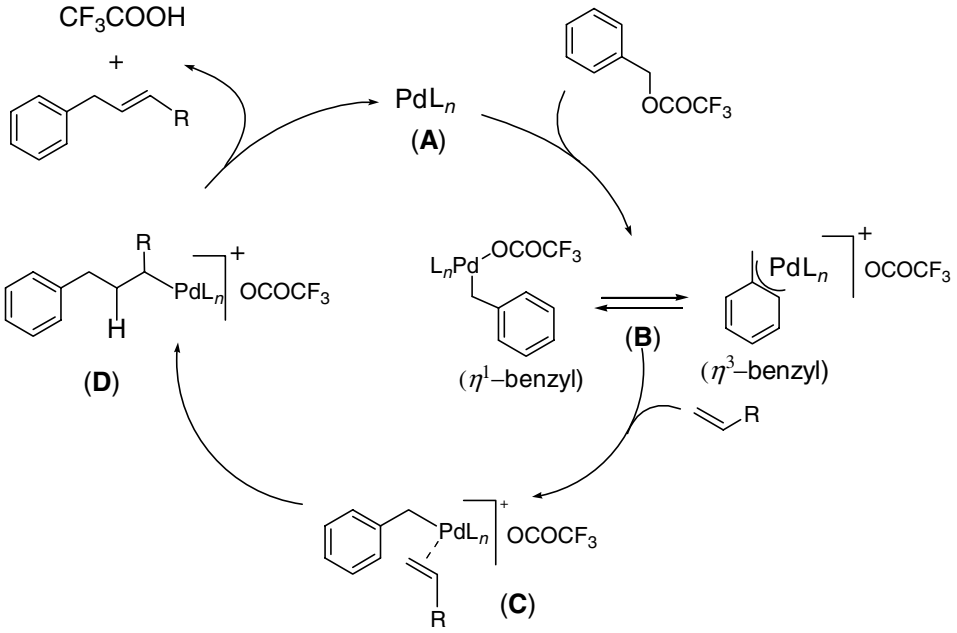
The palladium-catalyzed benzylation can be also performed with olefins such as 2-vinylpyridine, 4-methylstyrene, 4-chlorostyrene, and 1,1-diphenylstyrene, whereas acrylonitrile did not react with benzyl trifluoroacetate.

3. Discussion

3.1. Proposed mechanism for the palladium-catalyzed benzylation of olefins

On the basis of fundamental studies described above on the reaction of Pd(0) complexes with benzyl carboxylates and on the reactions of the benzylpalladium complexes toward olefins, we propose a catalytic cycle to account for the mechanism of the present palladium-catalyzed benzylation of olefins as shown in Scheme 4.

Since the Pd(0) complexes in combination with tertiary phosphines act as the catalysts for the benzylation reaction,

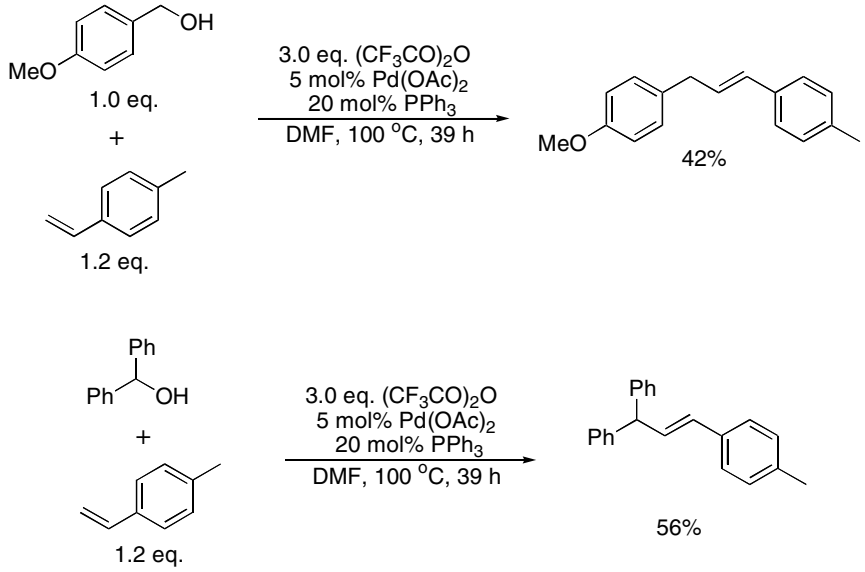


Scheme 4. Proposed mechanism for palladium-catalyzed olefin benzylation.

it is reasonable to assume the Pd(0) species (**A** in Scheme 4) at the start of the catalytic cycle [43]. As was established in the studies on the oxidative addition of benzyl carboxylates with Pd(0) complexes, the C–O bond in benzyl carboxylate is cleaved on interaction with a Pd(0) complex to give benzylpalladium carboxylate (**B**). The oxidative addition of the electron-rich Pd(0) complexes to give benzylpalladium intermediate seems to occur more readily in the reaction with more electronegative benzyl carboxylates. The model studies revealed that the benzylpalladium trifluoroacetate species is in an equilibrium between the neutral and ionic forms, which may have solvent-coordinated η^1- or η^3-benzylic forms.

The olefin will approach and coordinate to the benzylpalladium species **B** giving **C** which undergoes insertion of the coordinated olefin into the benzylpalladium bond to give the alkylpalladium complex **D**. The experimental results that the olefin insertion takes place more readily with the benzyl trifluoroacetate than with benzoate or nicotinate suggest the involvement of dissociation of the CF_3COO^- ligand to provide a coordination site for the incoming olefin.

After the usual *syn* β-H abstraction to liberate the benzylated olefin and a Pd hydride species, CF_3COOH will be released into the solution with regeneration of the Pd(0) species **A** to carry the further catalytic cycle. A solvent like DMF may be serving to make the liberation of CF_3COOH easier by having an interaction with the acid. The ready release of the carboxylic acid may help driving the catalytic



Scheme 5. Direct benzylation of *p*-methylstyrene with benzylic alcohols.

cycle by hindering the re-insertion of the produced olefin into the Pd–H bond formed in the β-H abstraction. An alternative route to the β-H elimination by palladium is the direct hydrogen abstraction by the CF_3COO^- anion.

3.2. Development of catalytic processes using benzylic alcohols in the presence of anhydride

As we described earlier in Scheme 2, the direct conversion of carboxylic acids into aldehydes or ketones could be accomplished in the presence of an external anhydride or dicarbonate such as pivalic anhydride or dimethyl dicarbonate without preparing the anhydride of the carboxylic acid.

By application of the similar concept, we examined if benzylic alcohols could be utilized directly for benzylation of olefins without using the preformed benzylic esters. Treatment of *p*-methoxybenzyl alcohol with *p*-methylstyrene at 100 °C in DMF in the presence of trifluoroacetic anhydride (3 equiv.) and a palladium catalyst for 24 h gave the benzylation product of *p*-methylstyrene. Similarly, substitution of *p*-methylstyrene with diphenylmethanol could be achieved (Scheme 5).

These results indicate the possibility of further expansion of the present methodology to olefination of various benzylic alcohols without prior preparation of benzylic carboxylates.

4. Conclusion

We have developed a novel and practical method for accomplishing catalytic substitution of olefins with benzylic groups affording arylalkyl-2-alkenes by using palladium catalysts. The method has been developed on the basis of fundamental studies on cleavage of C–O bond in benzylic esters on their interaction with a Pd(0) complex to give benzyl(carboxylato)palladium complexes. The method does not require the use of organic halides nor of a base, thus providing an advantage over the conventional Mizoroki–Heck process where organic halides are used in combination with bases producing byproducts as waste.

Examination of properties of the isolated benzyl palladium trifluoroacetate complexes that are assumed as the reaction intermediate in the catalytic cycle revealed that the benzylpalladium trifluoroacetate exists as an equilibrium mixture of neutral η^1- and ionic η^3-benzylpalladium complexes and the ionic η^3-form is favored in polar media. It was established that the benzylpalladium trifluoroacetate reacted with ethyl acrylate to afford the Mizoroki–Heck product by insertion of the olefin into the benzylpalladium bond followed by β-H abstraction.

These results support the proposed mechanistic cycle in Scheme 4, which is constituted of elementary processes comprising (1) oxidative addition of a benzylic ester to a Pd(0) complex to give a benzylpalladium carboxylate, (b) coordination of an olefin to the benzylpalladium species, (c) insertion of the coordinated olefin into the benzylpalladium bond, and (d) β-H elimination to liberate the benzylated olefin. Utility of the present palladium-catalyzed benzylation method for synthesis of various useful organic compounds has been demonstrated.

5. Experimental

All manipulations were carried out under argon using Schlenk tube techniques. Solvents were purified by the usual methods under argon. Benzylic trifluoroacetates were synthesized by the reaction of trifluoroacetic anhydride with corresponding benzyl alcohols in the presence of triethylamine. The palladium complexes, $[Pd(PPh_3)_4]$ [44] $[Pd(PCy_3)_2]$ [45], $[Pd(dba)_2]$ [46], *trans*-$[Pd(CH_2Ph)Cl(PMe_3)_2]$ [47], $[Pd(CH_2Ph)(OCOCF_3)(PMePh_2)]$ [6], and $[Pd(CH_2Ph)OCOCF_3(PMe_3)_2]$ [6] were prepared by the reported procedures. NMR spectra were recorded on JEOL Lambda 500 or 400 spectrometers for ^1H (referenced to $SiMe_4$ via residual solvent protons), $^{13}C\{^1H\}$ (referenced to $SiMe_4$ via the solvent resonance) and $^{31}P\{^1H\}$ (referenced to 85% H_3PO_4 as an external standard). Coupling patterns are expressed by d (doublet), t (triplet), vt (virtual triplet), q (quartet), sep (septet), and m (multiplet). Low-resolution mass spectra were obtained with a JEOL JMS-Automass 150 that is coupled with a gas chromatograph. FAB mass analysis and elemental analysis were performed by the Material Characterization Central Laboratory of Waseda University. Assignment of the NMR signals of benzyl palladium complexes was made by comparison with the related benzylic palladium complexes [48].

5.1. Preparation of trans-$[Pd(CH_2Ph)(OCOPh)(PMe_3)_2]$ (**3a**)

Styrene (0.31 ml, 2.01 mmol) was added to a mixture of acetone (5 ml) and *trans*-$[PdEt_2(PMe_3)_2]$ (**1a**, 424.0 mg, 1.33 mmol) at −20 °C. The mixture was stirred at 50 °C for 2 h to give a homogeneous yellow solution. After cooling the solution at room temperature, benzyl benzoate (0.27 ml, 1.41 mmol) was added to this solution and the solution was stirred at 50 °C for 4 h. On concentrating the solution, hexane was added to the solution to yield a white precipitate, which was filtered and collected. Subsequent washing with hexane and drying in vacuo gave a pale white powder of *trans*-$[Pd(CH_2Ph)(OCOPh)(PMe_3)_2]$ (390.0 mg, 0.83 mmol, 59% yield, based on benzyl benzoate). ^1H NMR ($CDCl_3$, 500 MHz, 293 K) δ 8.12–7.14 (m, 10H, aromatic H), 2.63 (t, $J = 7$ Hz, 2H, CH_2Ph), 1.3 (vt, $J = 3$ Hz, 18H, PMe_3). ^{13}C NMR ($CDCl_3$, 125 MHz, 293 K) δ 171.6 (s, Ph*C*OO), 147.7 (s), 147.6 (s), 137.4 (s), 129.8 (s), 129.5 (m), 127.7 (s), 127.5 (s), 124.0 (s, aromatic C), 13.2 (m CH_2Ph), 13.1 (vt, $J = 14$ Hz, 18H, PMe_3). ^{31}P NMR ($CDCl_3$, 202 MHz) δ −13.3 (s, PMe_3). FAB-MS. Found: 470.08 (M), Calc. for $C_{20}H_{30}O_2P_2Pd$: 470.08 (M). Anal. Calc. for $C_{20}H_{30}O_2P_2Pd$: C, 51.02; H, 6.42. Found: C, 51.10; H, 6.31%.

5.2. Preparation of trans-(benzyl)(nicotinato)bis(trimethylphosphine)palladium (**3b**)

Styrene (0.47 ml, 4.11 mmol) was added to a mixture of acetone (5 ml) and *trans*-[$PdEt_2(PMe_3)_2$] (642.0 mg, 2.03 mmol), at −20 °C. On stirring the mixture at 50 °C for 2 h, the mixture became homogeneous. After cooling this yellow solution at room temperature, benzyl nicotinate (0.42 ml, 2.34 mmol) was added to this solution and the solution was stirred at room temperature for 24 h. On concentrating the solution, hexane was added to the solution to yield a white precipitate, which was filtrated and collected. Subsequent washing with hexane and drying in vacuo gave a white powder of *trans*-(benzyl)(nicotinato)bis(trimethylphosphine)palladium (777.0 mg, 1.65 mmol, 71% yield based on benzyl nicotinate). ^{1}H NMR (CD_2Cl_2, 500 MHz) $\delta = 9.20$ (d, $J = 1$ Hz, 1H, nicotinate H), 8.64 (dd, $J = 1$, 5 Hz, 1H, nicotinate H), 8.29 (dt, $J = 1$, 1, 8 Hz, 1H, nicotinate H), 7.53 (d, $J = 8$ Hz, 2H, phenyl H), 7.35 (dd, $J = 5$, 8 Hz, 1H, nicotinate H), 7.27 (t, 8 Hz, 2H, phenyl H), 7.15 (t, $J = 8$ Hz, 1H, phenyl H), 2.66 (t, $J = 7$ Hz, 2H, CH_2Ph), 1.28 (vt, $J = 3$ Hz, 18H, PMe_3). ^{13}C NMR ($CDCl_3$, 125 MHz, 293 K) δ 169.8 (s), 151.3 (s), 150.7 (s), 147.5 (s), 136.9 (s), 132.7 (s), 129.6 (m), 127.9 (s), 124.3 (s), 122.9 (s, phenyl and nicotinate C), 13.5 (m, *C*H_2Ph) 13.2 (t, $J = 4$ Hz, PMe_3). ^{31}P NMR ($CDCl_3$, 202 MHz) δ −13.0 (s, *P*Me_3). FAB-MS. Found: 471.07 (M), Calc. for $C_{19}H_{29}NO_2P_2Pd$: 471.07 (M). Anal. Calc. for $C_{19}H_{29}NO_2P_2Pd$: C, 48.37; H, 6.20; N, 2.97. Found: C, 47.58; H, 6.36; N, 2.79%.

5.3. Preparation of trans-[Pd(CH$_2$Ph)Cl(PMePh$_2$)$_2$] (**5**)

To a mixture of benzene (10 ml) and *trans*-[$PdEt_2$(P-$MePh_2)_2$] (2.20 g, 3.89 mmol), styrene (1.40 ml, 12.21 mmol) was added at −20 °C. On stirring at 50 °C for 2 h, the mixture became a homogeneous yellow solution. After cooling the solution at room temperature, benzyl chloride (9.90 ml, 86.03 mmol) was added and the solution obtained was stirred at room temperature for 10 h. On concentrating the solution in vacuo, hexane was added to the solution to yield a white precipitate, which was filtered and collected. Subsequent washing with hexane and drying in vacuo gave a pale white powder of *trans*-[$Pd(CH_2Ph)Cl(PMePh_2)_2$] (2.01 g, 3.31 mmol, 85% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.51–7.35 (m, 20H, aromatic H), 6.83–6.36 (m, 5H, aromatic H), 2.47 (m, 2H, CH_2Ph), 1.3 (m, 6H, P*Me*Ph_2). ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz, 293 K) δ 12.4 (s, *P*$MePh_2$). FAB-MS. Found: 632.08 (M), Calc. for $C_{33}H_{33}ClP_2Pd$: 632.08 (M). Anal. Calc. for $C_{33}H_{33}ClP_2Pd$: C, 62.57; H, 5.25. Found: C, 62.02; H, 5.12%.

5.4. Preparation of (η^3-benzyl)bis(methyldiphenylphosphine)palladium hexafluorophosphate (**4**)

To an acetone solution (20 ml) of *trans*-[$Pd(CH_2Ph)$-$Cl(PMePh_2)_2$] (518.0 mg, 0.82 mmol), $AgPF_6$ (206.9 mg, 0.82 mmol) in 2 ml of acetone was added at −20 °C to give immediately a white suspension. The suspension was stirred for 2 h at −20 °C. Removal of AgCl by filtration gave a clear yellow solution. After its concentration followed by addition of ether, a yellow precipitate was formed. Filtration of the precipitate and the subsequent washing with ether and hexane and drying in vacuo gave a pale yellow powder of (η^3-benzyl)bis(methyldiphenylphosphine)palladium hexafluorophosphate (515 mg, 0.69 mmol, 85% yield). ^{1}H NMR ($CDCl_3$, 500 MHz, 253 K) δ 7.36–6.67 (m, 25H, aromatic H), 3.01 (d, $J = 9$ Hz, 2H, CH_2), 1.97 (d, $J =$ 10 Hz, 3H, P*Me*Ph_2), 1.23 (d, $J = 8$ Hz, 3H, P*Me*Ph_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 293 K) δ 133.3, 132.2, (m), 132.9, 131.8, 131.7 (m), 131.5.31.3, 131.1 (m), 130.5 (m) 130.4 (m), 129.0 (m), 128.8 (m), 120.5 (m), 117.3 (m), 59.4 (dd), $J = 6.41$, 38.95 Hz, 14.5, (d, $J = 30.12$ Hz), 10.89 (d, $J = 29.4$ Hz), 10.89 (d, $J = 24.4$ Hz). ^{31}P NMR ($CDCl_3$, 202 MHz, 253 K) δ 16.5 (d, $J = 44$ Hz, *P*$MePh_2$), 6.22 (d, $J = 44$ Hz, *P*$MePh_2$), −142.9 (sept., $J = 710$ Hz, PF_6^-). Anal. Calc. for $C_{33}H_{33}F_6P_3Pd$: C, 53.35; H, 4.48. Found: C, 53.28; H, 4.56%.

5.5. Preparation of [Pd(CH$_2$Ph)Cl(dppe)] (**6**)

To a mixture of benzene (20 ml) and *trans*-[$Pd(CH_2Ph)$-$Cl(PMePh_2)_2$] **4** (656.0 mg, 1.04 mmol), dppe (413.3 mg, 1.04 mmol) was added at room temperature. On standing the mixture at room temperature for 3 days, a yellow precipitate was formed from the solution. The precipitate was filtered, washed with ether (5 ml × 5) and dried in vacuo to give a yellow powder (536.0 mg, 0.85 mmol, 82% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.82–6.80 (m, 25H, aromatic H), 3.2 (dd, $J = 4$, 11 Hz, 2H, PhCH_2), 2.42–2.32, 2.02–1.92 (m, 4H, PC_2H_4P). ^{13}C{^{1}H} ($CDCl_3$, 125 MHz, 293 K) δ 147.4, 147.3, 133.8, 133.2, 132.6, 132.0, 131.0, 128.5, 128.4, 128.0, 127.0, 122.5, 34.25 (dd, $J = 3.14$, 94.11 Hz), 31.46 (dd, $J = 23.87$, 33.48 Hz), 23.21 (dd, $J = 10.38$, 24.91 Hz). ^{31}P NMR ($CDCl_3$, 202 MHz) δ 55.64, 33.14 (d, $J = 40$, PC_2H_4P). Anal. Calc. for $C_{33}H_{31}ClP_2Pd$: C, 62.77; H, 4.95. Found: C, 62.09; H, 4.85%.

5.6. Reaction of (benzyl)(trifluoroacetato)bis(methyldiphenylphosphine)palladium (**3**) with ethyl acrylate

To a DMF solution (3 ml) of (benzyl)(trifluoroacetato)-bis(methyldiphenylphosphine)palladium **3** (66.6 mg, 0.094 mmol) was added ethyl acrylate (0.0121 ml, 0.133 mmol). The mixture was stirred for 24 h at 80 °C. After the mixture was cooled to room temperature, the solvent was evaporated in vacuo. The yield of ethyl (*E*)-4-phenyl-2-butenoate (**7**) was determined as 25% by ^{1}H NMR using $C_2H_2Cl_2$ as an internal standard. Characterization of **7** was made by GC–MS and NMR. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.22–7.11 (m, 5H, aromatic H), 6.91 (dt, $J = 6$, 15 Hz, 1H, CH_2CHCH), 4.00 (q, $J = 7$ Hz, 2H, OCH_2CH_3), 3.45 (d, $J = 6$ Hz, 2H, CH_2CHCH), 1.08 (t, $J = 7$ Hz, 3H, OCH_2CH_3). GC-MS *m*/*z* (rel intensity) 190 (47), 145 (38), 117 (100), 91 (77), 77 (9).

5.7. Reaction of (η^3-benzyl)bis(methyldiphenylphosphine)-palladium hexafluorophosphate (**4**) with ethyl acrylate

To a $CHCl_3$ solution (5 ml) of (η^3-benzyl)bis(diphenylmethylphosphine)palladium hexafluorophosphate (226.0 mg, 0.304 mmol) was added ethyl acrylate (0.040 ml, 0.372 mmol). The mixture was stirred for 24 h at 80 °C. After the mixture was cooled to room temperature, the solvent was evaporated in vacuo. The yields of ethyl (*E*)-4-phenyl-2-butenoate (**7**) and of ethyl (*E*)-4-phenyl-3-butenoate (**8**) were determined by ^{1}H NMR using $C_2H_2Cl_2$ as an internal standard (the sum of the yields of **7** and **8** was 62%).

5.8. Palladium-catalyzed olefin benzylation with benzyl trifluoroacetate

The general procedure for the reaction is shown below. A DMF solution (5 ml) containing benzyl trifluoroacetate (1.00 mmol), olefin (1.20 mmol), $Pd(OAc)_2$ (0.05 mmol) and PPh_3 (0.20 mmol) was placed in a 25 ml Schlenk tube. The solution was stirred at 100 °C for 39 h. On cooling the mixture, ethyl acetate and water were added and the aqueous layer was extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ and the solvent was evaporated in vacuo. Purification of the residue on column chromatography (hexane/ethyl acetate as the elute) gave the benzylation compound.

5.8.1. Entry 1 of Table 5

Colorless oil (75%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.22–7.11 (m, 5H, aromatic H), 6.91 (dt,$J = 6$, 15 Hz, 1H, CH_2CHCH), 4.00 (q, $J = 7$ Hz, 2H, OCH_2CH_3), 3.45 (d, $J = 6$ Hz, 2H, CH_2CHCH), 1.08 (t, $J = 7$ Hz, 3H, OCH_2CH_3). GC–MS *m*/*z* (rel intensity) 190 (47), 145 (38), 117 (100), 91 (77), 77 (9). Anal. Calc. for $C_{19}H_{22}O_3$: C, 75.76; H, 7.42. Found: C, 75.30; H, 7.37%.

5.8.2. Entry 2 of Table 5

Colorless oil (59%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.11–7.05 (m, 3H, aromatic H and CH_2CHCH), 6.85 (d, $J = 8$ Hz, 2H, aromatic H), 5.78 (d, $J = 16$ Hz, 1H, CH_2CHCH), 4.17 (q, $J = 7$ Hz, 2H, $COOCH_2CH_3$), 3.79 (s, 3H, O*Me*), 3.46 (d, $J = 7$ Hz, 2H, CH_2CHCH), 1.27 (t, $J = 7$ Hz, 3H, $COOCH_2CH_3$). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.5 (s), 158.4 (s), 147.7 (s), 129.8 (s), 129.7 (s), 122.1 (s), 114.1 (s), 60.2 (s), 55.3 (s), 37.6 (s), 14.2 (s). FAB-MS. Found: 220.11(M), Calc. for $C_{19}H_{22}O_3$: 220.11 (M). Anal. Calc. for $C_{19}H_{22}O_3$: C, 70.89; H, 7.32. Found: C, 70.12; H, 7.38%.

5.8.3. Entry 3 of Table 5

Colorless oil (65%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.24–7.13 (m, 9H, aromatic H), 6.41 (d, $J = 16$ Hz, 1H, CH_2CHCH), 6.28 (dt, $J = 7$, 16 Hz, 1H, CH_2CHCH), 3.51 (d, $J = 7$ Hz, 2H, CH_2CHCH), 2.30 (s, 3H, *Me*). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 140.3 (s), 136.8 (s), 134.7 (s), 130.9 (s), 129.2 (s), 128.6 (s), 128.4 (s), 128.2 (s), 126.2 (s), 126.0 (s), 39.2 (s), 21.1 (s). FAB-MS. Found: 208.13 (M), Calc. for $C_{19}H_{22}O_3$: 208.13 (M). Anal. Calc. for $C_{19}H_{22}O_3$: C, 92.26; H, 7.74. Found: C, 92.09; H, 7.32%.

5.8.4. Entry 4 of Table 5

Colorless oil (42%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.24–7.13 (d, $J = 8$ Hz, 2H, aromatic H), 7.14 (d, $J = 9$ Hz, 2H, aromatic H), 7.08 (d, $J = 8$ Hz, 2H, aromatic H), 6.85 (d, $J = 9$ Hz, 2H, aromatic H), 6.39 (d, $J = 16$ Hz, 1H, CH_2CHCH), 6.27 (dt, $J = 7$, 16 Hz, 1H, CH_2CHCH), 3.78 (s, 3H, O*Me*), 3.47 (d, $J = 7$ Hz, 2H, CH_2CHCH), 2.31 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.1 (s), 136.8 (s), 134.8 (s), 132.4 (s), 130.6 (s), 129.6 (s), 129.2 (s), 128.6 (s), 126.0 (s), 113.9m (s), 55.3 (s), 38.4 (s), 21.1 (s). FAB-MS. Found: 238.14 (M), Calc. for $C_{17}H_{18}O$: 238.14 (M). Anal. Calc. for $C_{20}H_{30}O_2P_2Pd$: C, 85.67; H, 7.61. Found: C, 85.18; H, 7.28%.

5.8.5. Entry 5 of Table 5

Colorless oil (81%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ7.29–7.24 (m, 2H, aromatic H), 7.17–7.16 (m, 2H, aromatic H), 7.12–7.10 (m, 2H, aromatic H), 7.19–7.17 (m, 2H, aromatic H), 6.43–6.39 (d, $J = 16$ Hz, 1H, CH_2CHCH), 6.28–6.21 (dt, $J = 7$, 16 Hz, 1H, CH_2CHCH), 3.50 (d, $J = 7$ Hz, 2H, CH_2CHCH), 2.34 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz) δ138.8 (s), 137.0 (s), 134.5 (s), 131.9 (s), 130.0 (s), 129.2 (s), 128.6 (s), 127.5 (s), 38.6 (s), 21.1 (s). FAB-MS. Found: 242.09 (M), Calc. for $C_{16}H_{15}Cl$: 242.09, Anal. Calc. for $C_{16}H_{15}Cl$: C, 79.17; H, 6.23. Found: C, 79.31; H, 6.02%.

5.8.6. Entry 6 of Table 5

Colorless oil (80%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.02–6.96 (m, 2H, aromatic H), 7.13–7.09 (m, 2H, aromatic H), 7.19–7.16 (m, 2H, aromatic H), 7.25–7.23 (m, 2H, aromatic H), 2.32 (m, 3H, CH_3), 3.50–3.48 (d, $J = 6.71$ Hz, 2H, $F(C_6H_4)CH_2CH$), 6.31–6.22 (m, $J = 7$ Hz, $J = 14$ Hz, 1H, $CH_2CHCH(C_6H_4)CH_3$), 6.43–6.38 (m,$J = 14$ Hz, 1H, $CH_2CHCH(C_6H_4)CH_3$). ^{13}C{^{1}H}NMR ($CDCl_3$, 125 MHz) δ 160.5 (s), 137.0 (s), 135.9 (s), 134.6 (s), 131.1 (s), 130.0 (s), 129.2 (s), 127.9 (s), 126.0 (s), 115.1 (s), 38.5 (s), 21.1 (s). FAB-MS. Found: 226.12 (M) Calc. for $C_{16}H_{15}F$: 226.12. Anal. Calc. for $C_{16}H_{15}F$: C, 84.92; H, 6.68. Found: C, 84.69; H, 6.46%.

5.8.7. Entry 7 of Table 5

Colorless oil (27%); ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K) δ 8.51 (d, $J = 4$ Hz, 1H, 2-pyridine H), 7.53 (m, 1H, 2-pyridine H), 7.25–7.12(m, 6H, 2-pyridine H + Ph H), 7.02 (m, 1H, 2-pyridine H), 6.80 (dt, $J = 7$, 16 Hz, 1H, CH_2CHCH), 6.45 (d, $J = 16$ Hz, 1H, CH_2CHCH), 3.53 (d, $J = 7$ Hz, 2H, CH_2CHCH). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.9 (s), 149.5 (s), 139.6 (s), 136.3 (s), 134.2 (s), 131.3 (s), 128.8 (s), 128.6 (s), 126.3 (s), 121.8 (s), 121.1 (s), 39.2 (s). GC–MS *m*/*z* (rel intensity) 78 (25), 93 (100), 118 (58), 167 (12), 180 (10), 195 (87). FAB-MS. Found: 196.11 (M + H), Calc. for $C_{19}H_{22}O_3$: 195.10(M).

5.8.8. Entry 8 of Table 5

Colorless oil (21%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.23–6.75 (m, 14H, aromatic H), 6.17 (t, $J = 8$ Hz, 1H, CH_2CH), 3.71 (s, 3H, O*Me*), 3.33 (d, $J = 8$ Hz, 2H, CH_2CH). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.0 (s), 142.5 (s), 142.2 (s), 139.9 (s), 133.0 (s), 130.0 (s), 129.3 (s), 128.3 (s), 128.2 (s), 128.1 (s), 127.3 (s), 127.1 (s), 114.0 (s), 55.3 (s), 35.0 (s). FAB-MS. Found: 300.15 (M), Calc. for $C_{17}H_{18}O$: 300.15 (M). Anal. Calc. for $C_{20}H_{30}O_2P_2Pd$: C, 87.96; H, 6.71. Found: C, 88.05; H, 6.76%.

5.8.9. Entry 9 of Table 5

Colorless crystal (58%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.15–7.13 (m, 2H, aromatic H), 6.86–6.84 (m, 2H, aromatic H), 7.23–7.22 (m, 2H aromatic H), 7.21 (m, 2H aromatic H), 3.73 (s, 3H, OCH_3), 3.46–3.45 (d, $J = 6$ Hz, 2H, $CH_3O(C_6H_4)CH_2CH$), 6.37–6.27 (m, 2H, $CH_2CHCH(C_6H_4)Cl$). ^{13}C NMR ($CDCl_3$, 125 MHz) δ158.2 (s), 136.0 (s), 132.6 (s), 131.8 (s), 130.5 (s), 129.5 (s), 128.6 (s), 127.3 (s), 114.0 (s), 55.2 (s, $CH_3O(C_6H_4)$), 38.4 (s, $CH_3O(C_6H_4)CH_2CHCH$). FAB-MS. Found: 258.08 (M), Calc. for $C_{16}H_{15}ClO$: 258.08 (M). Anal. Calc. for $C_{16}H_{15}ClO$: C, 74.27; H, 5.84. Found: C, 74.39; H, 5.68%.

5.8.10. Entry 10 of Table 5

Colorless oil (69%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.12–7.10 (m, 2H, aromatic H), 7.18–7.16 (m, 2H, aromatic H), 6.86 (m, 2H, aromatic H), 6.43–6.40 (m, 1H, CH_2CHCH), 6.29–6.21 (m, 2H, CH_2CHCH), 3.51–3.49 (m, 12 H, CH_3), 3.42 (m, 2H, CH_2CHCH). ^{13}C NMR ($CDCl_3$, 125 MHz) δ136.6 (s), 135.4 (s), 134.9 (s), 133.3 (s), 130.0 (s), 129.1 (s), 128.9 (s), 126.7 (s), 125.9 (s), 32.5 (s), 21.1 (s), 20.8 (s), 19.9 (s). FAB-MS. Found: 250.17 (M), Calc. for $C_{19}H_{22}$: 250.17 (M). Anal. Calc. for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found: C, 91.00; H, 9.00%.

5.8.11. Entry 11 of Table 5

Colorless oil (56%); ^{1}H NMR ($CDCl_3$, 400 MHz, r.t.) δ 7.26 (d, $J = 8$ Hz, 2H, aromatic H), 7.11 (d, $J = 8$ Hz, 2H, aromatic H), 6.45 (s, 2H, aromatic H), 6.42 (m, 1H, CH_2CHCH), 6.28 (m, 1H, CH_2CHCH), 3.84 (s, 6H, *m*-O*Me*), 3.83 (s, 3H, *p*-O*Me*), 3.47 (m, 2H, CH_2CHCH), 2.33 (s, 3H, *Me*). ^{13}C NMR ($CDCl_3$, 125 MHz, 293 K) δ 153.3 (s), 137.0 (s), 136.1 (s), 134.7 (s), 131.1 (s), 129.3 (s), 127.9 (s), 126.1 (s), 105.8 (s), 60.9 (s), 56.2 (s), 39.7 (s), 21.1 (s). FAB-MS. Found: 298.16 (M), Calc. for $C_{19}H_{22}O_3$: 298.16 (M). Anal. Calc. for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43. Found: C, 76.04; H, 7.47%.

X-ray data: The detailed crystallographic information is described in a CIF file deposited in CCDC No.638734.

5.9. Palladium-catalyzed olefin benzylation from benzyl alcohols

In a general procedure for the reactions, a DMF solution (5 ml) of benzyl alcohol (1 mmol), trifluoroacetic anhydride (3.00 mmol). olefin (1.20 mmol), $Pd(OAc)_2$ (0.05 mmol) and PPh_3 (0.20 mmol) was placed in a 25 ml Schlenk tube. The solution was stirred at 100 °C for 39 h. On cooling the mixture, ethyl acetate and water were added and the aqueous layer was extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ and the solvent was evaporated in vacuo. Purification of the residue by column chromatography (hexane/ethyl acetate) gave benzylation compound.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.10.051.

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