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Palladium–dppb–borate-catalyzed regioselective synthesis of cinnamate esters by alkoxycarbonylation of phenylacetylene

Jimoh Tijani, Rami Suleiman and Bassam El Ali*

The regioselective alkoxycarbonylation of phenylacetylene into various cinnamate esters was achieved with a catalyst system formed from palladium (II), 1,4-bis(diphenylphosphino) butane (dppb) and salicylborate complex in acetonitrile as a solvent. The influence of various parameters on the overall conversion of phenylacetylene and the selectivity of the reaction were studied systematically by varying the type of palladium complex, acids promoter, CO pressure, temperature and the reaction time. This investigation allowed us to obtain the predominant formation of cinnamate esters with excellent selectivity (90–96%).

Keywords: alkoxycarbonylation; phenylacetylene; cinnamate esters; unsaturated esters; salicylic acid; boric acid; palladium; phosphine

Introduction

The synthesis of carboxylic esters from easily available starting materials is one of the basic reactions in synthetic chemistry. The use of carbon monoxide as a 'carboxyl-source' in palladium-catalyzed hydroalkoxylcarbonylation reaction is a widely known methodology for the synthesis of esters.[1,2] Cinnamic acid and its esters are important intermediates for the production of pharmaceuticals, fragrances, light-sensitive and electrically conductive materials and agrochemicals.[3] Cinnamate esters are made conventionally through Claisen condensation from benzaldehyde and alkylacetate in the presence of sodium alkoxide[4] or by esterification of cinnamic acid,[5] or by using palladium acetate–tertiary phosphine as a catalyst in the reaction of phenyl bromide and an alkyl acrylate.[6]

Many publications and patents disclose oxidative carbonylation of olefins to α,β-unsaturated esters by reacting an olefin with carbon monoxide, oxygen, and an alcohol in the presence of palladium and copper salts.[3,7–9] The disadvantages of these methods are a large excess of oxidant (copper (II) salt),[10] and lack of selectivity due to many side products.[3]

Alkoxycarbonylation of phenylacetylene with alcohols normally gives *trans*- and *gem*-α,β-unsaturated esters [**1** and **2**; Eq. (1)]. The ratio of these products strongly depends on the catalytic system and the reaction conditions employed.[11–15] The regioselective synthesis of the *gem*-α,β-unsaturated ester **2** has been achieved by various methods.[14,16–19] However, there is only one report that describes the regioselective alkoxycarbonylation of phenylacetylene into *trans*-α,β-unsaturated esters (89%) using the cationic palladium complex [(Pd(dppf)(PhCN)]BF_4.[11]

We have previously reported successful methods for the production of α,β-unsaturated acid derivatives via thiocarbonylation,[20] alkoxycarbonylation[12] and aminocarbonylation of different alkynes.[19–21] The recent report on palladium-borate-catalyzed methoxycarbonylation of alkenes[22] encouraged us to investigate the effect of salicylborate on the one-step synthesis of cinnamic acid esters by palladium-catalyzed regioselective alkoxycarbonylation of phenylacetylene [Eq. (1)].

Experimental Section

Materials

Phenylacetylene, palladium catalysts, phosphine ligands and acids were purchased from Aldrich and were used without further purification. The alcohols and the solvents were distilled and dried before use. ^{1}H and ^{13}C NMR spectra were recorded on a 500 MHz Joel 150 NMR machine. Chemical shifts were reported in ppm relative to tetramethyl silane (TMS) using $CDCl_3$. The products of the reactions were analyzed on a gas chromatograph HP-6890-plus equipped with a 30 m capillary column (HP-1) and also on a GC-MS Varian Saturn 2000 equipped with a 30 m capillary column (HP-5).

General procedure for the hydroesterification of phenylacetylene with alcohols

A mixture of $Pd(OAc)_2$ (0.02 mmol), 1,4-bis(diphenylphosphino)butane (0.08 mmol), boric acid (0.3 mmol), salicyclic acid (0.6 mmol), phenylacetylene (2.0 mmol) and alcohol (8.0 mmol) in 10 ml of acetonitrile was placed in the glass liner, equipped with a stirring bar and fitted in a 45 ml Parr autoclave. The autoclave was purged three times with carbon monoxide and pressurized with 200 psi of CO. The mixture was stirred and heated for the required time. After cooling the pressure was released, and the mixture was diluted with ethyl ether, washed with water and dried with anhydrous $MgSO_4$. The conversion of phenylacetylene and the selectivities of the products were analyzed by GC using 100 µg of anisole as standard. The distribution of products was analyzed by ^{1}H NMR.

* *Correspondence to: Bassam El Ali, King Fahd University of Petroleum & Minerals, Chemistry Department, 31261 Dhahran, Saudi Arabia.*
E-mail: belali@kfupm.edu.sa

King Fahd University of Petroleum & Minerals, Chemistry Department, 31261 Dhahran, Saudi Arabia

Results and Discussion

The regioselective synthesis of *gem*- or *trans*-α,β-unsaturated ester was achieved by the direct carbonylation of phenylacetylene with methanol catalyzed by palladium (II) in the presence of a diphosphine ligand and suitable additives. The reaction conditions were optimized and the effects of various reaction parameters on the activity and selectivity were determined.

Effect of the type of palladium complex

The activity and the selectivity of various palladium catalysts and their effects on the selectivity of the catalytic alkoxycarbonylation of phenylacetylene with methanol were studied and the results are summarized in Table 1. The reaction was carried out by adding the required amount of the palladium complex, dppb, salicylic acid, boric acid and methanol in 10 ml acetonitrile under CO (200 psi) at 90 °C for 3 h. Conversions higher than 96% were obtained with $Pd(OAc)_2$, $Pd(NO_3)_2$, $Pd(SO_4)_2$ and Pd/C. However, palladium catalysts containing chloride ions gave no products under the reaction conditions, whereas $Pd(CN)_2$ gave only 12%. It seems that the presence of ligands having higher binding ability such as chloride (Table 1, entries 6–8) reduces the availability of the coordination sites around palladium, leading to lower catalytic activity.[23,24] This is probably related to the strong interaction of the chloride ion with the active center compared with the relatively easy replacement of NO_3^-, SO_4^{2-} and OAc^- anions by the bidentate phosphine ligand. A salicylborate complex (BSA) is probably formed *in-situ* between boric and salicyclic acid [Eq. (2)].[22]

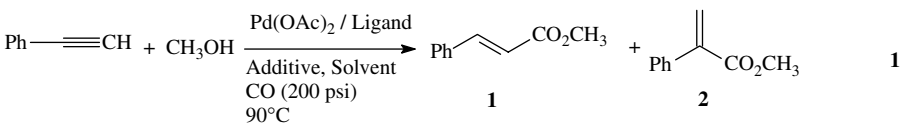
Effect of the type of ligand

The effects of the type of ligand on the conversion and the selectivity toward both *trans*- and *gem*-α,β-unsaturated ester were investigated. Different bidentate phosphine ligands with wide range of bite angles and also monodentate phosphine ligands were used in the study. The results summarized in Table 2 showed an increase in the conversion of phenylacetylene and in the selectivity toward *trans*-α,β-unsaturated ester (methyl cinnamate) with the increase in the bite angle of the ligands. A correlation between diphosphine ligand bite angle, rate and selectivity was observed. Dppe, 1,2-bis(diphenylphosphino)ethane, with a bite angle of 85, gave only 3% conversion of phenylacetylene into mainly styrene, while dppf, 1,1′-bis-(diphenylphosphino)ferrocene, and dppp [1,3-bis(diphenylphosphino)propane], with bite angles 96° and 91°, gave conversions of 99 and 88% and selectivities in the *trans* isomer **1** of 86 and 76%, respectively. A further increase in the bite angle to 98° in dppb, 1,4-bis(diphenylphosphino)butane, led to a total conversion and a selectivity of 92% in methyl cinnamate. The only exception was observed with BINAP, 2,2′-bis(diphenylphosphino)methyl-1,1′binaphthyl, and BIPHEN, 2,2′-bis-(diphenylphosphino)methyl-1,1′biphenyl, which is probably related to the narrow flexibility range and more rigid backbone that reduces the range of bite angle.[21] A similar correlation between the increase in bite angles of diphosphine ligands and the rate or selectivity was also reported in the hydrocarboxylation of styrene[25] and carbonylative coupling of aniline with 1-heptyne.[21]

The major reasons for these variations in the conversion and selectivity toward the *trans* isomer **1** are related to both steric and electronic effects of the ligands, with the steric effect seeming to be the major determinant in this catalytic system. The steric nature of the catalytic intermediate ensures that the hydropalladation process exhibits high regioselectivity, resulting in *cis*-addition of Pd complex to a less hindered carbon atom, which finally yields the *trans* isomer **1**. In dppp and dppb, the organic backbone is bent out of the plane of coordination and, in contrast, a skew conformation is observed for dppe. In dppp and dppb complexes, the phenyl groups can bend away from the remaining two coordination sites.[26,27] Flexible backbones also impose low energy barriers for the variation of the P–Pd–P angle and Pd–P distances. Moreover, theoretical calculations indicate that such flexibility may enhance migration reactions.[28,29]

Extended Huckel calculations indicate that, in the diphosphine complexes with small ligand bite angles, the electron density is shifted to the hydride ligand.[30] Therefore, the increase in the bite angle of the ligand increases the hydride ligand acidity, hence the basicity of the following ligands increases in the order:

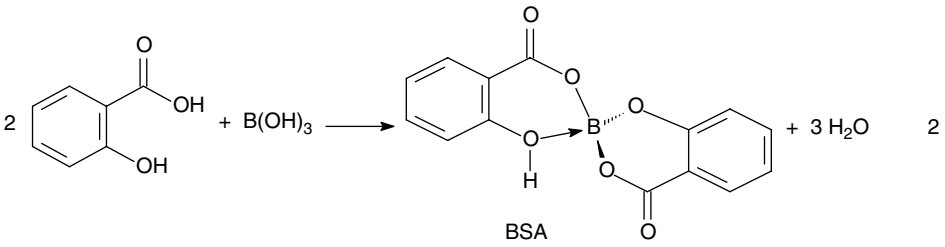
Table 1. Alkoxycarbonylation of phenylacetylene by [Pd]_dppb–BSA. Effect of the type of palladium catalyst[a]



Entry	Palladium catalyst	Conversion[b] (%)	1 : 2[c] (%)
1	$Pd(OAc)_2$	99	92 : 8
2	$Pd(NO_3)_2$	99	84 : 16
3	$Pd(SO_4)_2$	98	91 : 9
4	Pd/C (5%)	97	90 : 10
5	$Pd(CN)_2$	12	97 : 3
6	$PdCl_2$	Traces	–
7	$Pd(PhCN)_2Cl_2$	0	–
8	$Pd(PPh_3)_2Cl_2$	0	–

[a] Reaction conditions: [Pd], 0.02 mmol; dppb, 0.08 mmol; phenylacetylene, 2.0 mmol; $B(OH)_3$, 0.30 mmol; salicylic acid, 0.60 mmol; methanol, 8.0 mmol; CH_3CN, 10.0 ml; CO, 200 psi; 90 °C; 3 h.
[b] Determined by GC.
[c] Determined by GC and ^1H NMR.

Table 2. Alkoxycarbonylation of phenylacetylene by $Pd(OAc)_2$–ligand–BSA. Effect of the type of ligand[a]



Entry	Ligand	Bite angle	Conversion[b] (%)	1 : 2[c] (%)
1	dppb	98	100	92 : 8
2	dppf	96	99	86 : 14
3	dppp	91	88	76 : 24
4	BIPHEN	92	100	46 : 54
5	BINAP	92	99	34 : 66
6[d]	dppe	85	3	–
7[e]	Bu_3P	–	11	20 : 80
8	PPh_3	–	24	14 : 86

[a] Reaction conditions: $Pd(OAc)_2$, 0.02 mmol; ligand, 0.08 mmol; phenylacetylene, 2.0 mmol; $B(OH)_3$, 0.30 mmol; salicylic acid, 0.60 mmol; methanol, 8.0 mmol; CH_3CN, 10.0 ml; CO, 200 psi; 90 °C; 3 h.
[b] Determined by GC.
[c] Determined by GC and ^1H NMR.
[d] 3% Styrene.
[e] 6% Styrene.

dppe > dppp > dppb. This order suggests a possible reason for the reduced activity of dppe.[30]

It was suggested that ready availability of two coordination sites is crucial to the possible formation of active cationic palladium complex in the alkoxycarbonylation of phenylacetylene.[31] Another key to the formation of *trans* isomer may be the ability of dppb to coordinate to palladium through one or both phosphine atoms depending on the circumstances, inferring the result that dppb is effective whereas dppe is almost ineffective for this carbonylation process.[32–34]

Basic monophosphine ligand such as PBu_3 show less catalytic activity with 11% conversion and 80% selectivity in *gem* isomer **2** (Table 2, entry 7). Similarly, low conversion (24%) of phenylacetylene and higher selectivity (86%) for the *gem* isomer **2** were observed when triphenylphosphine was used as a ligand (Table 2, entry 8).

Effect of the ratio of dppb:$Pd(OAc)_2$

The ratio of dppb:$Pd(OAc)_2$ was also found to have a significant role on the catalyst activity and the selectivity of the reaction (Fig. 1). The conversion increased from 66% (dppb:[Pd] = 1), to 100% (dppb:[Pd] = 2) and the total conversion was maintained up to a ratio of dppb:[Pd] of 5, after which the conversion decreased significantly (51%). The selectivity in *trans* ester **1** increased from 70 to 90% then to 92% and finally remained at 92% at a dppb:[Pd] ratio of 1, 2, 4 and 5, respectively. Substantial decomposition of the active catalyst into palladium metal was observed only with the ratio dppb:[Pd] = 1. The use of excess ligand probably increased the steric and electronic density around the palladium center so that the equilibrium shifted in the direction of *pro-trans* intermediate.

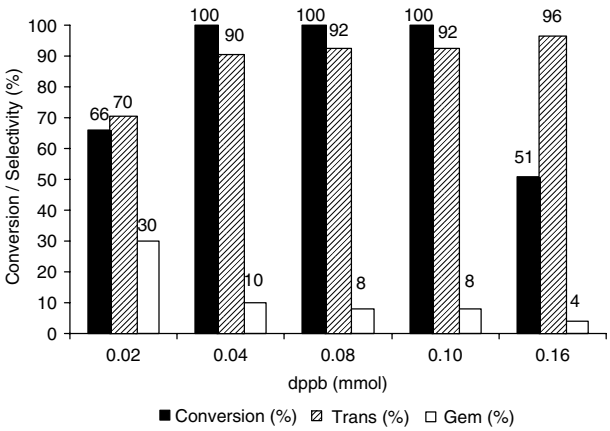


Figure 1. Alkoxycarbonylation of phenylacetylene with methanol by $Pd(OAc)_2$–dppb–BSA. Effect of the amount of ligand. Reaction conditions: $Pd(OAc)_2$, 0.02 mmol; phenylacetylene, 2.0 mmol; methanol, 8.0 mmol; $B(OH)_3$, 0.30 mmol; salicylic acid, 0.60 mmol; CH_3CN, 10.0 ml; CO, 200 psi; 90 °C; 3 h (*trans* + *gem* = 100%).

Effect of the type and the amount of additives

Table 3 shows the effect of the type and the amount of additives on the catalytic alkoxycarbonylation of phenylacetylene with methanol. The presence of acid is necessary to form the catalytically active species. The results showed no reaction in the absence of salicylborate (BSA) (Table 3, entry 1). The catalytic activity was considerably low (10%) with 0.03 mmol of salicylborate, and complete conversions were obtained when the amounts of salicylborate were increased to 0.30 and 0.45 mmol (Table 3, entries 2–5). The results indicate that the acid should be present in significant excess to achieve maximum activity and

Table 3. Alkoxycarbonylation of phenylacetylene by $Pd(OAc)_2$–dppb. Effect of the type of additive[a]

Entry	Additive (mmol/mmol)	Conversion[b] (%)	1 : 2[c] (%)
1	–	0	–
2	$B(OH)_3$ – salicylic acid (0.03–0.06)	10	88 : 12
3	$B(OH)_3$ – salicylic acid (0.10–0.20)	91	85 : 15
4	$B(OH)_3$ – salicylic acid (0.30–0.60)	100	92 : 8
5	$B(OH)_3$ – salicylic acid (0.45–0.90)	100	91 : 9
6	Salicylic acid (0.60)	22	47 : 53
7	$B(OH)_3$ (0.30)	0	–
8	*p*-TSOH (0.30)	100	86 : 14
9	CH_3SO_3H (0.30)	100	89 : 11

[a] Reaction conditions: $Pd(OAc)_2$, 0.02 mmol; dppb, 0.08 mmol; phenylacetylene, 2.0 mmol; methanol, 8.0 mmol; CH_3CN, 10.0 ml; CO, 200 psi; 90 °C; 3 h.
[b] Determined by GC.
[c] Determined by ^1H NMR and GC.
[d] Boric salicylic acid (BSA) complex was preformed in CH_3CN for 1 h.

Table 4. Hydroesterification of phenylacetylene by $Pd(OAc)_2$–dppb–BSA. Effect of the type of solvent[a]

Entry	Solvent	Conversion[b] (%)	1–2[c] (%)
1	CH_3CN	100	92 : 8
2	PhCN	100	86 : 14
3	DMSO	100	18 : 82
4	DMF	96	12 : 88
5	Toluene	89	24 : 76
6	CH_2Cl_2	43	41 : 59
7	Hexane	35	39 : 61
8	THF	8	24 : 76
9	CH_3OH	32	30 : 70

[a] Reaction conditions: $Pd(OAc)_2$, 0.02 mmol; dppb, 0.08 mmol; phenylacetylene, 2.0 mmol; $B(OH)_3$, 0.30 mmol; salicylic acid, 0.60 mmol; methanol, 8.0 mmol; solvent, 10.0 ml; CO, 200 psi; 90 °C; 3 h.
[b] Determined by GC.
[c] Determined by GC and ^1H NMR.

selectivity (Table 3, entries 1–5). At lower acid concentrations and in the presence of excess of methanol, lower activities were observed.[35,36]

A decrease in both conversion and selectivity towards the *trans* isomer was observed when salicyclic acid alone was used as promoter (Table 3, entry 6). The total conversions obtained with sulfonic acid derivatives such as methanesulfonic and *p*-toluenesulfonic acid (Table 3, entries 8 and 9) encouraged us to pursue these systems further in order to improve both conversions and selectivities using a variety of alkyl and aryl alkynes.

The basic question concerns the role of the acid in this carbonylation reaction. The acid may react, forming metal hydride species through protonation of the electron-rich Pd(0) species [which is formed from *in situ* reduction of Pd(II) when heated in the presence of CO].[37] These species are electron-rich and known to form Pd–H in the presence of strong acid. The salicylborate anion can either coordinate to the metal center, forming a neutral complex, or act as a counter-anion to the cationic palladium species. The later is more plausible in the present system for three reasons: firstly, the coordination of the salicylborate anion would render it prone to hydrogenation of the alkynes to alkenes and alkanes;[38] secondly, the other reason is that weakly coordinating labile anions would be displaced from the sphere of metals by less labile ligands;[39] and finally, the weakly coordinating anions, because of their easier dissociation from ion-pair, would generate a more electrophilic palladium center.[40,41]

Effect of type of solvent

Table 4 contains the results of the effect of various solvents on the catalytic alkoxycarbonylation of phenylacetylene with methanol. No clear correlation was found between the conversion, the selectivity and the dielectric constant of the solvents. Non-coordinating solvent, such as *n*-hexane, dichloromethane and toluene, gave conversions of 35, 43 and 89% with the corresponding selectivities in *trans* isomer **1** of 39, 41 and 24%, respectively (Table 4, entries 5–7).

Almost complete conversions were obtained with polar, coordinating solvents such as acetonitrile, benzonitrile, DMF and DMSO (Table 4, entries 1–4). However, when methanol was used alone as a solvent and a nucleophile under similar conditions, only 32% conversion was obtained after 3 h of reaction (Table 4, entry 9). This may be due to the formation of less active palladium carbomethoxy.[35,36] As described earlier, the coordination of the anions to the cationic palladium center may depend strongly on the polarity of the reaction medium.[40] Solvation of the ion-pair by the polar solvents is expected to facilitate cation–anion dissociation and, therefore, renders the metal center more electrophilic and more easily accessible by the substrate molecules.[40]

Among all the solvents used, only acetonitrile and benzonitrile gave complete conversion and with the *trans*-α,β-unsaturated ester **1** formed as the major product. The reason for the high selectivity for the *trans* isomer exclusively in these solvents is not yet totally clear. It could be explained by the fact that acetonitrile is acting as both solvent and co-ligand.[3,42] In cationic complexes the fourth coordination position could be occupied by acetonitrile, which probably plays an active role in the migratory insertion.[43] It is apparent that the nucleophilic character of the co-ligand may remarkably affect the rate of conversion of $[Pd(P-P)H]^+$ into $[Pd(P-P)OMe]^+$ and hence promote the products of carbonylation whose formation required a Pd–H bond.[41] The influence of the co-ligand on the stability of the hydride metal initiator and hence on product selectivity has been reported for palladium-catalyzed enantioselective carbonylation of styrene.[44]

Effects of the temperature

A systematic study on the influence of the temperature on the regioselectivity and the catalytic activity in the alkoxycarbonylation of phenylacetylene with methanol was achieved at a variety of temperatures ranged from 70 to 110 °C (Fig. 2). The formation of the *trans*-α,β-unsaturated esters prevailed at all temperatures. An increase in the temperature, however, increased the amount of the *trans*-α,β-unsaturated ester up to 90 °C, above which the selectivity in *trans* ester **1** started to drop.

At higher temperature (110 °C), complete conversion was obtained while the selectivity for the *trans* isomer decreased to 78%; this decrease could be related to the displacement of phosphine by CO which is favored at higher temperature.[45] This makes the palladium center less crowded and therefore less selective for the *trans* isomer. Similarly, the lower temperature (80 °C) resulted in

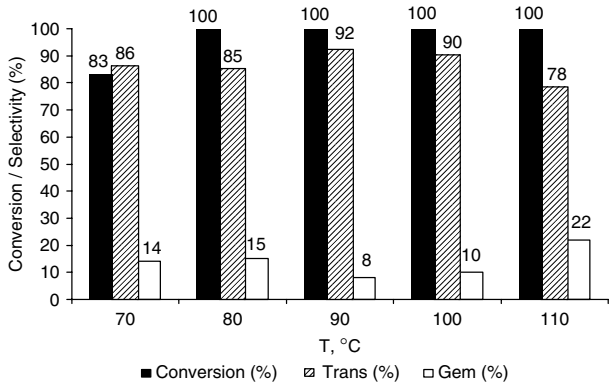


Figure 2. Alkoxycarbonylation of phenylacetylene with methanol by $Pd(OAc)_2$–dppb–BSA. Effect of the temperature. Reaction conditions: $Pd(OAc)_2$, 0.02 mmol; dppb, 0.08 mmol; phenylacetylene, 2.0 mmol; methanol, 8.0 mmol; $B(OH)_3$, 0.30 mmol; salicylic acid, 0.60 mmol; CH_3CN, 10.0 ml; CO, 200 psi; 3 h (*trans* + *gem* = 100%).

lower selectivity in *trans* isomer **1** with conversion remaining the same (100%). The conversion of phenylacetylene and the selectivity toward the *trans*-α,β-unsaturated ester were deteriorated as the reaction temperature decreased to 70 °C.

Alkoxycarbonylation of phenylacetylene with different alcohols

The effects of different alcohols as esterifying reagents (Equation 3) were studied and the results are presented in Table 5. The conversions and selectivities remained fairly constant with increasing numbers of carbons in the alcohol. This shows that the alkoxy mechanism is playing a minor role in this process because the initial formation of palladium carboalkoxy will be expected to decrease with the increase in the number of carbons of alcohols.[35,36,46]

Proposed mechanisms

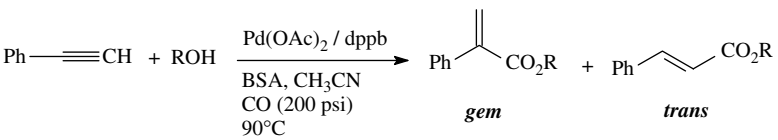
There are two main mechanisms that have been proposed for alkoxycarbonylation of alkynes with alcohol: the hydride and alkoxy mechanisms.[11,23,25,46,47] It was reported that the insertion of styrene into metal acyl bond led to *gem* products, while insertion into hydrides led to *trans* products.[48] Based on the analysis of the literature and the present experimental results, we tentatively proposed two schemes where the hydride mechanism plays represents the major route towards the *trans* product. This was clear from the promoting effect of a hydride source observed with acid (Table 3).[23,48]

The first step in the proposed mechanism was the formation of palladium hydride by the reaction of $Pd(OAc)_2$, dppb, CO and acid.[21] The coordination of alkyne to palladium center followed by the insertion of CO may give two possible intermediates A and A′, depending on the nature of the palladium center, polarity of the solvent, steric and electronic effect of the ligand.

A literature precedent describes that the regiochemistry can be attributed to mainly steric effects.[38] Thus the (dppb)Pd–H bond tends to add preferentially to the less crowded carbon, i.e. to the terminal carbon forming intermediate B. In the case of the intermediate A′, the chelating diphosphine ligand would place the Ph group of the alkyne closer to the ligand, and this interaction would increase with the backbone constrains. The interaction would further increase with the bite angle of the diphosphine ligand. In such circumstances, the intermediate B may be relatively more stable than the intermediate B′, and hence will result in the formation of B.[11,21] With the monodentate phosphine, the lower conversion and selectivity is related to the lower steric crowdedness and preference for the *trans* orientation of the monodentate phosphine ligand due to both steric and electronic reasons. It is well known that the *gem*–*trans* ratio is rapidly changed at high temperature and affected by the use of excess of ligand (Table 2, entries 7 and 8).[40]

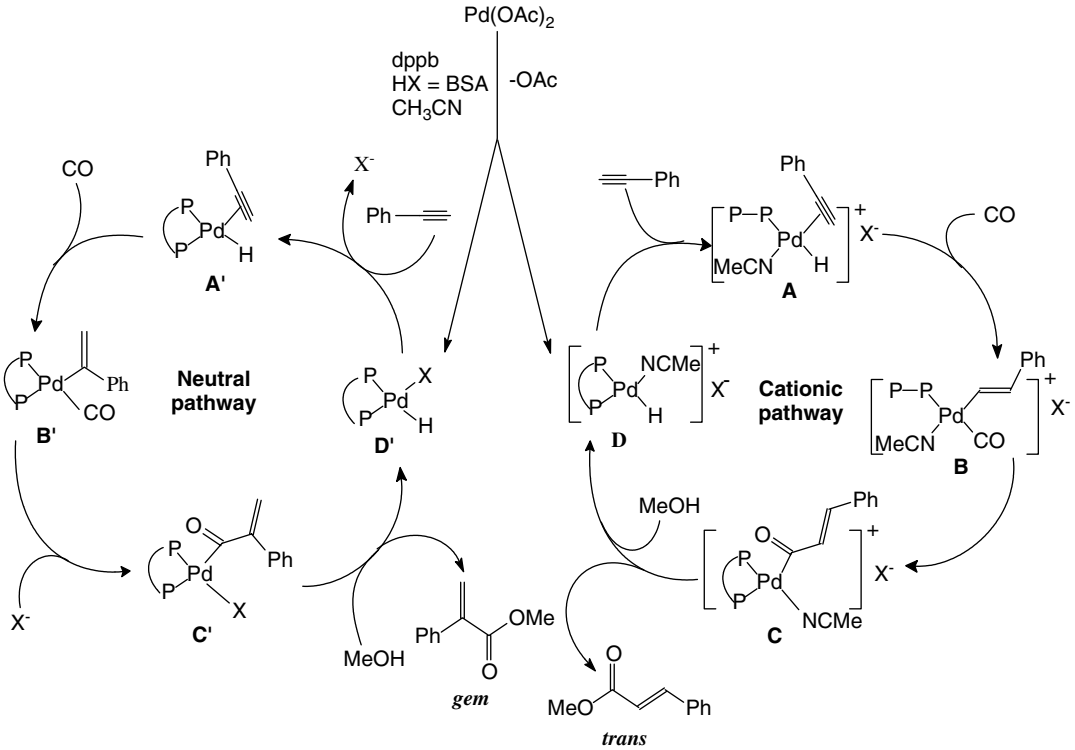
The charge distribution in phenylacetylene indicates that the terminal carbon is more nucleophilic than the internal carbon, because of the electron withdrawing effect of the phenyl group. Theoretical calculation (using Gaussian) gave the charge distribution as −0.452 for the terminal carbon and 0.094 for the internal carbon; therefore, it is expected that the terminal carbon of the triple bond will have more affinity for the cationic palladium

Table 5. Alkoxycarbonylation of phenylacetylene by [Pd]–dppb–BSA in the presence of different alcohols[a]



Entry	Alcohol ROH	Conversion[b] (%)	*trans*:*gem*[c] (%)
1	CH_3OH	100	92 : 8
2	CH_3CH_2OH	99	91 : 9
3	$CH_3(CH_2)_2OH$	99	92 : 8
4	$(CH_3)_2CHOH$	99	91 : 9
5	$CH_3(CH_2)_3OH$	99	91 : 9
6	$CH_3(CH_2)_4OH$	99	90 : 10
7	$CH_3(CH_2)_6OH$	100	89 : 11

[a] Reaction conditions: $Pd(OAc)_2$, 0.02 mmol; dppb, 0.08 mmol; phenylacetylene, 2.0 mmol; ROH, 8.0 mmol; $B(OH)_3$, 0.30 mmol; salicylic acid, 0.60 mmol; CH_3CN, 10.0 ml; 200 psi of CO; 90 °C; 3 h.
[b] Determined by GC.
[c] Determined by GC and ^1H NMR.



Scheme 1. Proposed mechanisms for the formation of the *gem* and *trans* products.

than the internal; hence more *trans* isomer will be expected in the cationic pathway then the neutral pathway.

Solvation by the polar solvents is expected to facilitate and stabilize cation–anion dissociation and therefore render the metal center more electrophilic and more easily accessible by the substrate molecules.[40] The neutral pathway is more stable in non-polar solvents, because of a close-contact ion-pair; this may be responsible for the lower activity and selectivity of the non-polar solvents. Claver and co-wokers have proposed that high *gem* selectivity proceed through a neutral catalytic cylce, while the *trans* preference follows a cationic catalytic cylce.[25]

In complex {Pd[^{13}C(O)Me(P–P′)MeCN](OTf) (P = PPh_2, P′ = $(toly)_2$}, no displacement of MeCN by ^{13}CO was observed at 1 atm.[40] A similar result had already been found for the complex [Pd[^{13}COMe(BINAPHOS)CD_3CN] (OTf).[49] Thermodynamic consideration may explain the stability of these palladium acyl complexes without the displacement of acetonitrile.

The reactions in DMF and DMSO gave *gem*-α,β-unsaturated ester selectively (Table 4, entries 3 and 4). The *gem* isomer was also produced when other alcohols such as 1-butanol and 2-propanol were used in place of methanol. Also the *gem*-α,β-unsaturated ester was produced as the major product when neat methanol was used in the absence of any other solvent. As already described in the literature, the formation of *gem* isomer was explained by the initial formation of carboalkoxy species (alkoxy mechanism).[34] CO Insertion into the palladium metal affords acylpalladium, and finally methanolysis of the acyl yields the final product.[34]

Conclusions

Palladium (II) and 1,4-bis(diphenylphosphino)butane in the presence of a mixture of salicylic and boric acids (BSA) and in acetonitrile was an effective and selective catalyst system for the regioselctive alkoxycarbonylation of phenylacetylene into *trans*-α,β-unsaturated ester (*trans*-methyl cinnamate). Polar co-ordinative solvents were found to be more active compared with the non-polar solvents or polar non-coordinative solvents. Acetonitrile was the most effective solvent for high selectivity toward the formation of *trans* isomer. This may be due to its ability to act as co-ligand with low binding affinity and also to stabilize palladium cationic species, which may be responsible for high selectivity towards *trans* isomers. Monophosphines as ligands in acetonitrile gave low conversion with *gem*-α,β-unsaturated ester as the major product. It was found that the suitable conditions for the formation of the *trans*-α,β-unsaturated ester appear to be the combined use of bulky diphosphines, acetonitrile and palladium cationic species as a catalyst. It was observed that the selectivity towards *trans* isomer was found to increase with the increase in bite angles of the diphosphine ligands.

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