Total regioselective control of the carbonylative coupling of 1-heptyne with aniline and *N*-methyl aniline catalyzed by palladium(II) and phosphine ligand

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Abstract

The carbonylative coupling of 1-heptyne (**1a**) with aniline (**2a**) has been successfully achieved in the presence of Pd(OAc)$_2$ and a suitable bidentate phosphine ligand and solvent. The *gem*-α,β-unsaturated amide (**3aa**) was formed as a predominant product in the presence of the catalytic system Pd(OAc)$_2$/1,3-bis(diphenylphosphino)propane (dppp)/*p*-toluenesulfonic acid (*p*-TsOH)/CO in THF as a solvent. While the use Pd(OAc)$_2$ and 1,4-bis(diphenylphosphino)butane (dppb), under syngas (CO/H$_2$) conditions and in CH$_2$Cl$_2$ as a solvent, affords the *trans*-α,β-unsaturated amide (**4aa**) as the major product. A minor cyclic product (**5aa**) was formed via the double carbonylation reaction. The regioselective carbonylative coupling reaction was also successfully applied to *N*-methyl aniline (**2b**) with 1-heptyne (**1a**) producing excellent yields of tertiary unsaturated amides.

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1. Introduction

The chemistry of saturated and unsaturated amides is still very attractive to both industry and academia due to the great importance of these organic compounds for academic research and industrial purposes [1]. The use of transition metal complexes in carbonylation chemistry represents a simple and efficient route for the production of various carbonyl compounds [2,3]. The classical method for the synthesis of *N*-aryl acrylamides was usually achieved by the reaction of aromatic amines with 2-subtituted acryloyl chlorides

or substituted acrylic acid [4]. The direct synthesis of 2-substituted acrylamides, important intermediates for polymer synthesis [5], from alkynes and amines, has earlier been reported using nickel [6,7], cobalt [8,9] and palladium [10,11] complexes.

Palladium complexes have been widely used in the carbonylation due to their high reactivity and selectivity. For example, the branched and linear α,β-unsaturated acids and their derivatives were produced by the palladium(II)-catalyzed carbonylation of alkynes where the regioselectivity depends strongly on the catalytic system and the reaction conditions [12–18]. However, the branched α,β-unsaturated acids or esters were formed as the major products in the most of cases.

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The carbonylation of alkynes into linear α,β-unsaturated acid derivatives as the major products by palladium catalysts have not been largely reported [19–21]. For example, a high selectivity (81%) of *trans*-methyl-2-octenoate (a linear α,β-unsaturated ester) was obtained by the carbonylation of 1-heptyne using Pd(II)/Sn(II)/PPh$_3$ [19]. Also Pd(dba)$_2$/1,4-bis-(diphenylphosphino)butane (dppb) was claimed to catalyze the carbonylation of terminal alkynes in the presence of formate esters producing the linear α,β-unsaturated esters as the major products [20]. Whereas Inoue and co-workers have used the palladium cationic complex [Pd(dppf)(PhCN)$_2$](BF$_4$)$_2$ to catalyze the carbonylation of terminal alkynes affording predominately the linear carboxylic esters [21]. Recently, we have described a new method for the production of linear α,β-unsaturated acid derivatives via the hydroesterification and the thio-carbonylation of various terminal alkynes in the presence of the catalytic system Pd(OAc)$_2$/dppb/CO/H$_2$ [22,23].

In this paper, we wish to report our study on the regioselective control of the catalytic synthesis of *gem*- and *trans*-α,β-unsaturated amides via the carbonylative coupling of 1-heptyne (**1a**) and aniline (**2a**). The effects of catalyst, ligand, solvent and other reaction parameters have been carefully studied in order to control the regioselectivity of the reaction toward the *gem*- or *trans*-α,β-unsaturated amides (**3aa** or **4aa**). *N*-Methyl aniline (**2b**) was also used as an aniline derivative to produce the tertiary *gem*- and *trans*-α,β-unsaturated amides (**3ab** or **4ab**) in high isolated yields and selectivity.

2. Experimental

2.1. Introduction

Aniline derivatives, alkynes, palladium catalysts, phosphine ligands and carboxylic acids are highly pure commercially available materials and were used without any further purification. Dry solvents have been used in all experiments. ^{1}H and ^{13}C NMR spectra were recorded on 500 MHz Joel l500 NMR machine. Chemical shifts (δ) were reported in ppm relative to tetramethyl silane (TMS) using CDCl$_3$. IR spectra were recorded on Perkin-Elmer 16F PC FT-TR

spectrometer and are reported in wave numbers (cm^{-1}). Gas chromatography (GC) analyses were realized on HP 6890 plus chromatography. Thin-layer chromatography (TLC) analyses were performed on silica gel Merck 60 F254 plates (250 μm layer thickness).

2.2. General procedure for the carbonylative coupling of terminal alkyl alkynes with aniline derivatives

A mixture of Pd(OAc)$_2$ (0.02 mmol), 1,3-bis(diphenylphosphino)propane (dppp; 0.04 mmol) or dppb (0.08 mmol), *p*-toluenesulfonic acid (*p*-TsOH; 0.12 mmol if used), 1-heptyne (2.0 mmol) and aniline (2.0 mmol) in 10 ml THF (or 10 ml CH$_2$Cl$_2$) was placed in the glass liner, equipped with a stirring bar, fitted in a 45 ml Parr autoclave. The autoclave was vented three times with CO and then pressurized at room temperature with 100 psi CO only in the system A (or pressurized with 300 psi CO and 300 psi H$_2$ in the system B). The mixture was stirred and heated for the required time. After cooling, the pressure was released, the reaction mixture filtered and the solvent was removed. The products were separated by preparative TLC (petroleum ether/acetone 10/1). The products were identified by ^{1}H and ^{13}C NMR, FT-IR, GC–MC and elemental analysis.

### 2.3. Spectra and analytical data for the synthesized α,β-unsaturated amides

2.3.1. N-Phenyl-2-pentylpropeneamide (3aa)
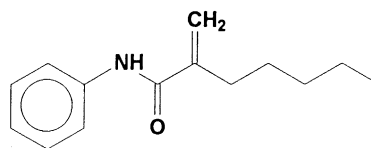
White crystal. m.p. = 59.6°. IR ν (cm^{-1}) KBr: 1656 (CO). ^{1}H NMR δ (ppm) CDCl$_3$: 0.90 (t, 3H, J = 6.7 Hz, CH$_2$CH$_3$), 1.31 (m, 4H, CH$_2$CH$_2$(CH$_2$)$_2$CH$_3$), 1.59 (m, 2H, CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$), 2.38 (t, 2H, J = 7.9 Hz, C=CCH$_2$CH$_2$), 5.36 (s, 1H, C=CH$_2$), 5.68 (s, 1H, C=CH$_2$), 7.08–7.58 (m, 5H, C$_6$H$_5$), 7.74 (s, 1H, NH). ^{13}C NMR δ (ppm) CDCl$_3$: 14.03, 22.46, 27.82, 31.46 32.42, 117.66, 120.05, 124.34, 128.97,

137.92, 146.49, 167.28 (CO). m/z 217 (M^+), Anal. calcd. for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.51; H, 8.63; N, 6.49.

2.3.2. (E)-N-Phenyl-2-octenamide (*4aa*)
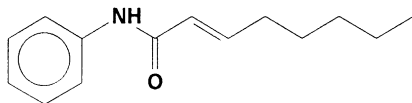
Oil. IR neat ν (cm^{-1}): 1666 (CO). ^{1}H NMR δ (ppm) CDCl$_3$: 0.90 (t, 3H, $J = 6.7$ Hz, CH$_2$C$\underline{H}_3$), 1.31 (m, 4H, C$\underline{H}_2$CH$_3$), 1.71 (m, 4H, CH$_2$(C$\underline{H}_2$)$_2$CH$_2$CH$_3$), 2.12 (q, CH=CHC$\underline{H}_2$), 5.91–5.94 (d, 1H, CH=C$\underline{H}$–CO, $J = 15.25$ Hz), 6.92–6.95 (m, 1H, C$\underline{H}$=CH–CO), 7.09–7.70 (m, 5H + 1H, C$_6\underline{H}_5$ + N$\underline{H}$). ^{13}C NMR δ (ppm) CDCl$_3$: 13.81, 22.29, 22.38, 27.8, 31.19, 31.53, 31.99, 34.44, 121.48, 123.72, 129.00, 136.00, 146.75, 164.80 (CO). m/z 217 (M^+). Anal. calcd. for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.31; H, 8.93; N, 6.47.

### 2.3.3. N,N-Methyl phenyl-2-pentylpropeneamide (*3ab*)
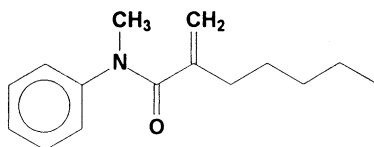
Oil. IR (neat) ν (cm^{-1}): 1640 (CO). ^{1}H NMR δ (ppm) CDCl$_3$: 0.86 (t, 3H, $J = 7.3$ Hz, CH$_2$C$\underline{H}_3$), 1.17–1.40 (m, 6H, CH$_2$(C$\underline{H}_2$)$_3$CH$_3$), 2.05 (t, 2H, $J = 7.95$ Hz, C=CC$\underline{H}_2$), 3.35 (s, 3H, N–C$\underline{H}_3$), 5.03 (s, 2H, C=C$\underline{H}_2$), 7.13–7.35 (m, 5H, C$_6\underline{H}_5$). ^{13}C NMR δ (ppm) CDCl$_3$: 13.97, 22.41, 27.14, 31.37, 33.67, 37.79, 117.97, 126.76, 126.84, 129.12, 144.49, 145.36, 171.87 (CO). m/z 231 (M^+). Anal. calcd. for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05. Found: C, 77.95; H, 9.35; N, 6.19.

2.3.4. N,N-Methyl phenyl-2-octeneamide (*4ab*)
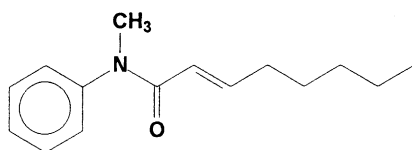
Oil. IR (neat) ν (cm^{-1}): 1650 (CO). ^{1}H NMR δ (ppm) CDCl$_3$: 0.76 (t, 3H, $J = 7.05$ Hz, C$\underline{H}_3$CH$_2$), 1.16 (m, 4H, C$\underline{H}_2$CH$_2$CH$_3$), 1.24 (m, 2H, CH$_2$C$\underline{H}_2$CH$_2$), 1.94 (t, 2H, $J = 7.95$ Hz, CHC$\underline{H}_2$), 3.24 (s, 3H, NC$\underline{H}_3$), 5.62 (d, 1H, COC$\underline{H}$=CHCH$_2$, $J = 15.25$ Hz), 6.81 (m, 1H, COCH=C$\underline{H}$CH$_2$), 7.04–7.32 (m, 5H, C$_6\underline{H}_5$). ^{13}C NMR δ (ppm) CDCl$_3$: 13.64, 22.03, 27.57, 30.89, 31.83, 37.05, 121.21, 126.99, 128.85, 129.18, 166.05. m/z 231 (M^+). Anal. calcd. for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05. Found: C, 77.65; H, 9.22; N, 6.25.
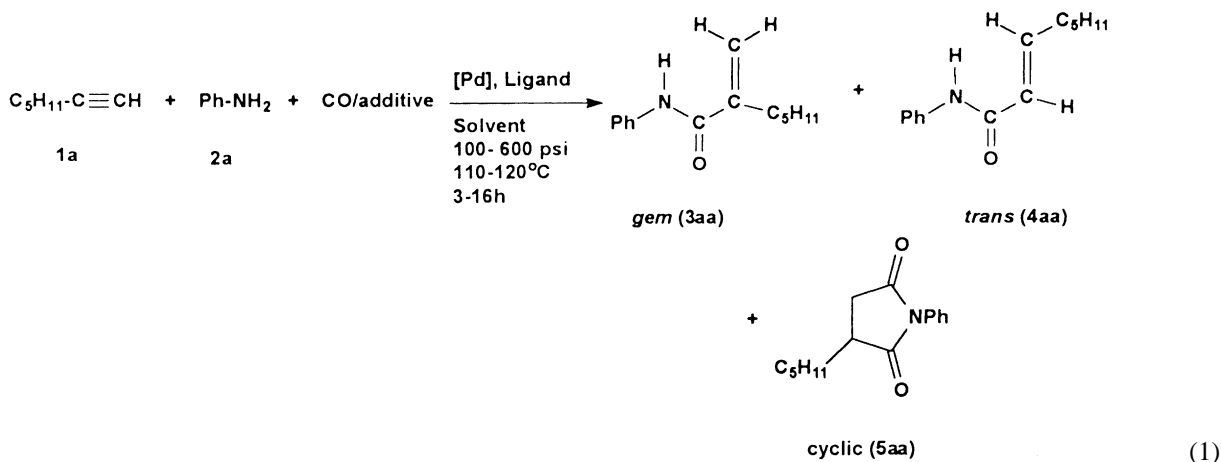
2.3.5. N-Phenyl-α-butylsuccinimide (*5aa*)
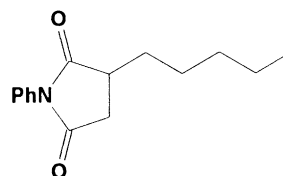
Oil. IR (neat) ν (cm^{-1}): 1706 and 1774 (CO). ^{1}H NMR δ (ppm) CDCl$_3$: 0.91 (t, 3H, $J = 6.7$ Hz, CH$_2$C$\underline{H}_3$), 1.35 (m, 2H, C$\underline{H}_2$CH$_3$), 1.45 (m, 2H, C$\underline{H}_2$CH$_2$CH$_3$), 1.65 (m, 4H, CH$_2$C$\underline{H}_2$C$\underline{H}_2$CH), 2.55–2.60 (dd, 1H, $J_1 = 4.25$ Hz, $J_2 = 3.15$ Hz, CHC$\underline{H}_2$), 2.95–2.99 (m, C$\underline{H}$CH), 3.01–3.05 (d, CHC$\underline{H}_2$, $J = 9.15$ Hz), 7.08–7.58 (m, 5H, C$_6\underline{H}_5$). ^{13}C NMR δ (ppm) CDCl$_3$: 13.98, 22.44, 26.35, 31.49, 34.58, 40.06, 122.50, 126.45, 128.58, 129.18, 132.04, 175.66, 179.23. m/z 245 (M^+).

3. Results and discussion

The synthesis of *gem*- or *trans*-α,β-unsaturated amides was achieved by the direct carbonylative coupling of terminal aliphatic alkyne (**1a**) with aniline (**2a**) using the system CO/*p*-TsOH/THF or CO/H$_2$/CH$_2$Cl$_2$. 1-Heptyne (**1a**) and aniline (**2a**) were used as model substrates to determine the optimum reaction conditions of the carbonylative coupling. The major products of the reaction are *N*-phenyl-2-pentylpropeneamide (**3aa**) and (*E*)-*N*-phenyl-2-octenamide (**4aa**). A small amount of the cyclic product (**5aa**) was detected in the reaction mixture under some experimental conditions (Eq. (1)).

$$C_5H_{11}-C\equiv CH \ + \ Ph-NH_2 \ + \ CO/additive \xrightarrow[\substack{\text{Solvent} \\ \text{100- 600 psi} \\ \text{110-120}^\circ\text{C} \\ \text{3-16 h}}]{\text{[Pd], Ligand}}$$

1a   **2a**

gem (**3aa**)   trans (**4aa**)

\+

cyclic (**5aa**)

(1)

3.1. Effect of the type of palladium complex

The presence of the metal catalyst is essential for the catalytic carbonylation of alkynes. Among the various transition metals used in the chemistry of carbonylation, palladium(0) and palladium(II) complexes showed the highest catalytic activity in the hydrocarboxylation reactions of alkenes and alkynes [2,10–12,21–23]. We have considered various palladium complexes in the reaction of carbonylative coupling of 1-heptyne (**1a**) and aniline (**2a**). The results are summarized in Tables 1 and 2.

The catalytic systems considered hereafter are denoted as A and B and consist of the following:

- system A = Pd/dppp/THF/*p*-TsOH/CO/120 °C/6 h;
- system B = Pd/dppb/CH$_2$Cl$_2$/CO/H$_2$/110 °C/16 h.

Pd(OAc)$_2$ showed the highest catalytic in the reaction of carbonylative coupling of 1-heptyne (**1a**) with aniline (**2a**) to produce selectively the *gem*- or *trans*-α,β-unsaturated amide (**3aa** or **4aa**) among the palladium catalysts employed. No reaction was observed under the experimental conditions of the system A but in the absence of either *p*-TsOH or

Table 1

Palladium(II)-catalyzed carbonylative coupling of 1-heptyne (**1a**) to aniline (**2a**). Effect of the type of palladium catalyst on the total yield and the selectivity of **3aa**[a]

Entry	Catalyst	CO (psi)	Additives	Yield (%)[b]	Selectivity (**3aa/4aa**, %)[c]
1	Pd(OAc)$_2$	100	–	Traces	–
2[d]	Pd(OAc)$_2$	100	*p*-TsOH	94	95/5
3[e]	Pd(OAc)$_2$	300	–	90	82/18
4	PdCl$_2$	100	*p*-TsOH	13	100/0
5	PdCl$_2$(PPh$_3$)$_2$	100	*p*-TsOH	23	100/0
6	PdCl$_2$(PhCN)$_2$	100	*p*-TsOH	12	48/52
7	Pd/C (10%)	100	*p*-TsOH	31	100/0
8	Pd(PPh$_3$)$_4$	100	*p*-TsOH	50	95/5
9[d]	Pd(OAc)$_2$(dppp)	100	*p*-TsOH	95	94/6
10	Pd(OTs)$_2$(dppp)	100	–	40	93/7

[a] Reaction conditions: catalyst (0.02 mmol), dppp (0.04 mmol), aniline (2.0 mmol), 1-heptyne (2.0 mmol), *p*-TsOH (0.12 mmol), THF (10 ml), 120 °C, 6 h.

[b] Isolated total yield.

[c] Determined by GC and ^{1}H NMR.

[d] 3 h.

[e] 300 psi of H$_2$ was used in place of *p*-TsOH.

Table 2
Palladium(II)-catalyzed carbonylative coupling of 1-heptyne (**1a**) to aniline (**2a**). Effect of the type of palladium catalyst on the total yield and the selectivity of **4aa**[a]

Entry	Catalyst	Yield (%)[b]	Selectivity (**3aa**/**4aa**, %)[c]
1	Pd(OAc)$_2$	90	18/82
2	PdCl$_2$	57	26/74
3	PdCl$_2$(PPh$_3$)$_2$	64	26/74
4	PdCl$_2$(PhCN)$_2$	45	27/73
5	Pd/C (10%)	61	24/76
6	Pd(PPh$_3$)$_4$	80	28/72
7[d]	Pd(OAc)$_2$(dppb)	41	42/58

[a] Reaction conditions: catalyst (0.02 mmol), dppb (0.08 mmol), aniline (2.0 mmol), 1-heptyne (2.0 mmol), CO (300), H$_2$ (300 psi), CH$_2$Cl$_2$ (10 ml), 110 °C, 16 h.
[b] Isolated total yield.
[c] Determined by GC and ^{1}H NMR.
[d] No dppb was added.

dppp (Table 1, entry 1). The carbonylative coupling carried out in the presence of Pd(OAc)$_2$ as a catalyst in the system A produced the unsaturated amides (**3aa** and **4aa**) in excellent total yield (94%) with *N*-phenyl-2-pentylpropeneamide (**3aa**) formed as a predominant product (95%) (Table 1, entry 2). The product (**3aa**) was the result of the carbonylative addition of aniline (**2a**) on the internal carbon of the triple bond of 1-heptyne (**1a**). The use of H$_2$ gas (in the absence of *p*-TsOH) under system A led to excellent total yield of products, but the selectivity toward **3aa** decreased to 82% (Table 1, entry 3). Surprisingly, the use of Pd(OAc)$_2$ in the system B led to interesting results of the selectivity in the reaction of carbonylative coupling of 1-heptyne (**1a**) and aniline (**2a**). The total yield of the products was maintained very high (90%) but the product (*E*)-*N*-phenyl-2-octenamide (**4aa**) was the predominant product of the reaction (82%) (Table 2, entry 1). The carbonylation catalyzed by different chloropalladium(II) complexes, such as PdCl$_2$, PdCl$_2$(PhCN)$_2$ and PdCl$_2$(PPh$_3$)$_3$ gave low yields of products (13–23%) under system A (Table 1, entries 4–6). The effect of Cl$^-$ was earlier reported to have a significantly influence on the catalytic activity of the palladium catalyst [24]. However, the same chloropalladium(II) complexes gave acceptable yields (45–57%) under the system B (Table 2, entries 2–4). The use of Pd/C (10%) under the conditions of the system A gave 31% isolated yield of **3aa** as the sole product and 61% of total yield under

system B conditions forming a mixture of **3aa**/**4aa** (24/76) (Table 1, entry 7; Table 2, entry 5). The palladium(0) complex (Pd(PPh$_3$)$_4$) is more sensitive to acidity than Pd(OAc)$_2$, which has been reflected by the lower yield of product; the total isolated yield obtained with Pd(PPh$_3$)$_4$ under system A was 50% only with excellent selectivity toward **3aa** (95%) (Table 1, entry 8). The total yield was significantly improved under system B where H$_2$ was used in place of *p*-TsOH to achieve 80% and forming a mixture of **3aa** and **4aa** with a ratio of 28/72 (Table 2, entry 6). In order to clarify and understand the mechanism of the reaction the complexes Pd(OAc)$_2$(dppp) and Pd(OTs)$_2$(dppp) were synthesized and tested in the carbonylative coupling of 1-heptyne (**1a**) and aniline (**2a**). Pd(OAc)$_2$(dppp) was used as a catalyst under the conditions of the system A but in the absence of any additional phosphine ligand, such as dppp (Table 1, entry 9). The results obtained are comparable to those obtained under system A with Pd(OAc)$_2$ as a catalyst (Table 1, entry 2). However, Pd(OTs)$_2$(dppp) used in the absence of dppp and *p*-TsOH gave only 40% of unsaturated amides (Table 1, entry 10). The addition of *p*-TsOH to the previous experiment involving Pd(OTs)$_2$(dppp) increased significantly the yields (>90%) of products. Therefore, these results explained the essential role of the acid *p*-TsOH in the formation and the stabilization of the cationic palladium hydride intermediate [(dpppPdH)$^+$OTs$^-$]. On the other hand, the complex Pd(OAc)$_2$(dppb) was also synthesized and used in the carbonylative coupling reaction under the conditions of the system B but in the absence of any additional amount of dppb. The yield and the selectivity of the unsaturated amides was much lower with the formation of palladium black at the end of the reaction due to the decomposition of the palladium complex (Table 2, entry 7). It seems very clear that the use of an additional amount of dppb is necessary for the stabilization of the palladium active intermediate species.

The regioselectivity of the reaction of carbonylative coupling of 1-heptyne (**1a**) and aniline (**2a**) is in favor of the *gem*-α,β-unsaturated amide (**3aa**) under the conditions of the system A involving Pd(OAc)$_2$/dppp/THF/*p*-TsOH/CO at 120 °C, whereas the *trans*-α,β-unsaturated amide (**4aa**) was formed under the conditions of the system B that includes Pd(OAc)$_2$/dppb/CH$_2$Cl$_2$/CO/H$_2$/110 °C.

3.2. Effect of the type of phosphine ligand

The results obtained previously indicated clearly that the introduction of bidentate phosphine ligand was necessary for the formation and the stabilization of the active catalyst species. The absence or the lack of a strong coordinating ligand may lead to the deactivation of the catalyst and the formation of inactive palladium black [25]. For instance, the use of monodentate phosphine ligands in place of dppp or dppb under the conditions of the system A or B gave poor results. For example, PPh$_3$ gave a poor yield (20%) of α,β-unsaturated amides and lower selectivity (*gem/trans* = 83/17). Other monophosphine ligands, such as P(*p*-C$_6$H$_4$CH$_3$)$_3$ and P(C$_6$H$_{11}$)$_3$ gave only traces of products.

An interesting correlation between the bite angle of the diphosphine ligand, the yield of products and the selectivity has been observed under the conditions of the system A (Fig. 1). For example, no reaction was observed when diphenylphosphinomethane (dppm) with very small bite angle (72°) was used as a ligand in place of dppp. Furthermore, 1,2-bis(diphenylphosphino)ethane (dppe) with a bite angle of 85° gave very low yield (6%) of amides, while dppp and (±)-2, 2′-bis(diphenylphosphino)-1,1′-binaphtyl (binap) with

bite angles 91 and 92° produced the unsaturated amides (**3aa** and **4aa**) with total yields of 95 and 81% and selectivity of **3aa** reaching 94 and 98%, respectively. Interestingly, a further increase in the bite angle to 98° with dppb and 1,5-bis(diphenylphosphino)pentane (dpppt) reduces the total yield to 59 and 23% and the selectivity for **3aa** to 78 and 82%, respectively.

The probably reason for the poor yield of dppm was the possible chelation to form unstable four-membered ring cyclic ligand–metal complex intermediate, which formed thermodynamically stable palladium alkenyl phosphorous ylide by insertion of alkyne into palladium–phosphine bond [26]. When we considered the flexibility of the bidentate ligands dppe, dppp and dppb to coordinate on the metal center, it may be seen that for dppp and dppb the organic backbone is bent out of the plane of coordination and that, in contrast, a skew conformation observed for dppe. In dppp and dppb complexes, the phenyl groups can bend away from the remaining two coordination sites [27,28]. Flexible backbones also impose low-energy barriers for the variation of the P–Pd–P angle and Pd–P distances. Moreover, theoretical calculations [29,30] indicate such flexibility may enhance migration reactions.

The lower catalytic activity of metal complex having dppb compared to dppp under the conditions of the
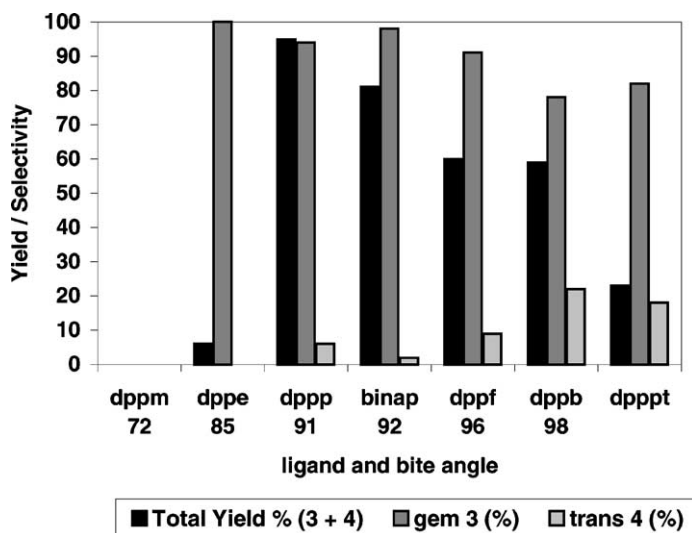

Fig. 1. Palladium(II)-catalyzed carbonylative coupling of 1-heptyne (**1a**) to aniline (**2a**). Effect of the bite angle of the phosphine ligand on the total yield and the selectivity of **3aa**. Reaction conditions: catalyst (0.02 mmol), dppp (0.04 mmol), aniline (2.0 mmol), 1-heptyne (2.0 mmol), CO (100 psi), *p*-TsOH (0.12 mmol), THF (10 ml), 120 °C, 3 h.

system A was attributed to the *trans* configuration of its oligomeric acyl complex (phenomenon which is not observed in neutral complex [27]). About half of the complex occurs in *trans* configuration in ionic dppb complex. A decrease in the rate of carbonylation for *trans* complex would be expected, since there is neither a CO in a *cis* to the coordinated alkenyl ligand as would required for a *cis* migration processes nor there is a phosphine *trans* to the Pd-alkenyl that can activate the migrating alkenyl group. A similar lower yield and selectivity of dpppt may also be connected to the *trans* effect which has been previously observed when n is equal to 6, 8, 10 and 12 $(Ph_2P(CH_2)_nPPh_2)$ [28,31].

A similar correlation between diphosphine ligand bite angle, catalytic efficiency and selectivity were observed in palladium(II)-catalyzed cross coupling reactions of Grignard reagents with organic halides. Hayashi and co-workers [32] found that the increase in reaction rate occurred with increase of ligand bite angles, the slowest was observed with dppe $(85°)$ and dppf $(96°)$ was found to be the most active. The selectivity of products decreases again if ligand with bite angle above $102°$ is employed.

The correlation between the type of diphosphine ligand and the bite angle has been studied under the conditions of the system B (Fig. 2). CO/H_2 was used in CH_2Cl_2 as a solvent leading to excellent total isolated yield of unsaturated amides and high selectivity toward the *trans*-α,β-unsaturated amide (**4aa**). The yield and the selectivity were found to increase with the bite angle of the ligand and reached maximum values with dppb then decreased again with dpppt. There are two possible reasons to explain these results. The first reason is related to an electronic effect; an increase in the ligand bite angle increases the hydride ligand acidity, which has been confirmed by extended Hückel calculation that indicates a shift in electron density toward the hydride ligand for diphosphine with small ligand bite angle [33,34]. The second and the more important reason is connected to a steric effect; an increase in ligand bite angle increases the steric crowdedness around the palladium complex, as the result hydrogen is added to the internal carbon of the terminal alkyne and subsequently leading to the formation of **3aa** versus **4aa**. Flexible backbones impose low-energy barriers for the variation of P–Pd–P angle and Pd–P distances [27].

3.3. Effect of the ratio of dppp/Pd(OAc)$_2$ and dppb/Pd(OAc)$_2$

Different ratios of dppp/Pd(OAc)$_2$ have been considered during the optimization of the reaction
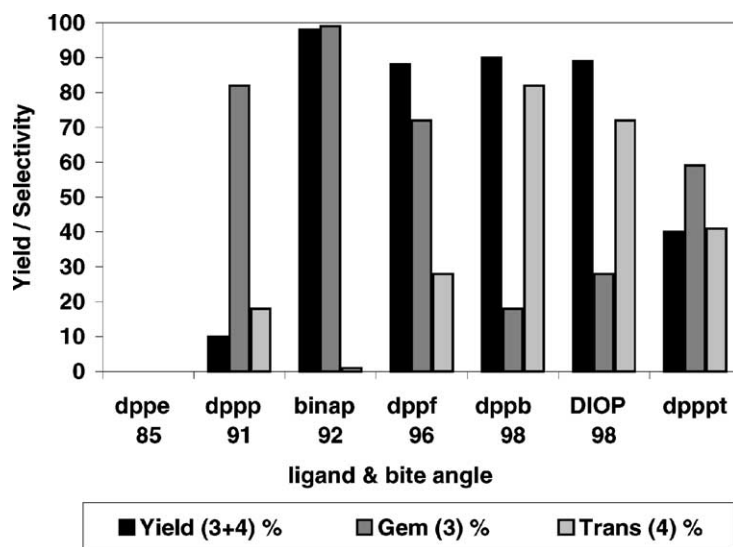

Fig. 2. Palladium(II)-catalyzed carbonylative coupling of 1-heptyne (**1a**) to aniline (**2a**). Effect of the bite angle of the phosphine ligand on the total yield and the selectivity of **4aa**. Reaction conditions: Pd(OAc)$_2$ (0.02 mmol), ligand (0.08 mmol), aniline (2.0 mmol), 1-heptyne (2.0 mmol), CO (300 psi), H$_2$ (300 psi), CH$_2$Cl$_2$ (10 ml), 110 °C, 16 h.
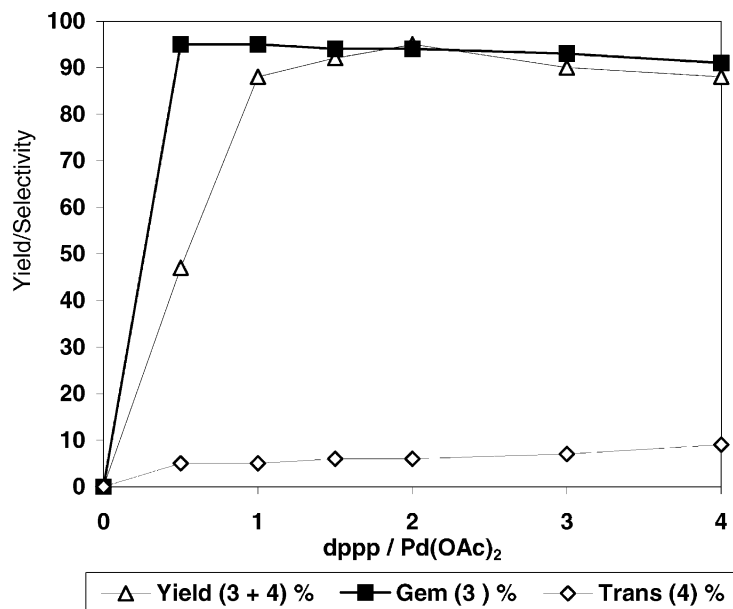
Fig. 3. Palladium(II)-catalyzed carbonylative coupling of 1-heptyne (**1a**) to aniline (**2a**). Effect of the molar ratio of dppp to Pd(OAc)$_2$ on the total yield and the selectivity of **3aa**. Reaction conditions: Pd(OAc)$_2$ (0.02 mmol), aniline (2.0 mmol), 1-heptyne (2.0 mmol), CO (100 psi), *p*-TsOH (0.12 mmol), THF (10 ml), 120 °C, 3 h.

conditions of the system A (Fig. 3). An optimal ratio of dppp/catalyst was found to be equal to two. A lower ratio resulted in the decrease of the total isolated yield of unsaturated amides due to the lack of sufficient amount ligand to stabilize the catalyst. The increase of the ratio had almost no effect on the outcome of the reaction.

Unlike the dppp, the amount of the diphosphine ligand dppb showed a significant effect on the total yield of the unsaturated amides (**3**aa + **4**aa) and the selectivity of **4aa** (Fig. 4) under the conditions of the system B. A steady increase in the total yield of **3**aa + **4**aa and the selectivity for **4aa** was observed with the increase in dppb/Pd ratio. The highest yield and selectivity was observed at a maximum molar ratio of four of dppb/Pd(OAc)$_2$. Any further addition of dppb resulted in drop of the yield and selectivity. In addition, a precipitation of metallic palladium was obtained at a ratio of dppb/Pd less than two.

The use of an excess of ligand increased probably the steric and electronic density at the palladium center so that the equilibrium was shifted toward the direction of pro-linear intermediate. The large excess of ligand

under the system B, where a syngas was used, was probably needed to prevent the coordination of all sites of palladium by a carbonyl group [35].

3.4. Effect of solvent

The study of the effect of the type of solvent showed no clear correlation between the dielectric constant of the solvent and the outcome of the reaction. Under the conditions of the system A, THF was found as the best solvent followed by toluene (Table 3, entries 1 and 3). Low yield and selectivity was observed with CH$_3$CN and CH$_2$Cl$_2$ (Table 3, entries 5 and 7). The same solvents were tested with the system B at the conditions of the formation of the *trans* product (**4aa**). Only traces of products were obtained with THF as a solvent (Table 3, entry 2). Toluene and CH$_3$CN gave either low yield or low selectivity of products (Table 3, entries 6 and 8). However, the best yield of products and selectivity of **4aa** was found in CH$_2$Cl$_2$ as a solvent. The reason for the high selectivity toward **4aa** exclusively in CH$_2$Cl$_2$ is not yet very clear to us. This effect can be related to high stability of the active catalytic
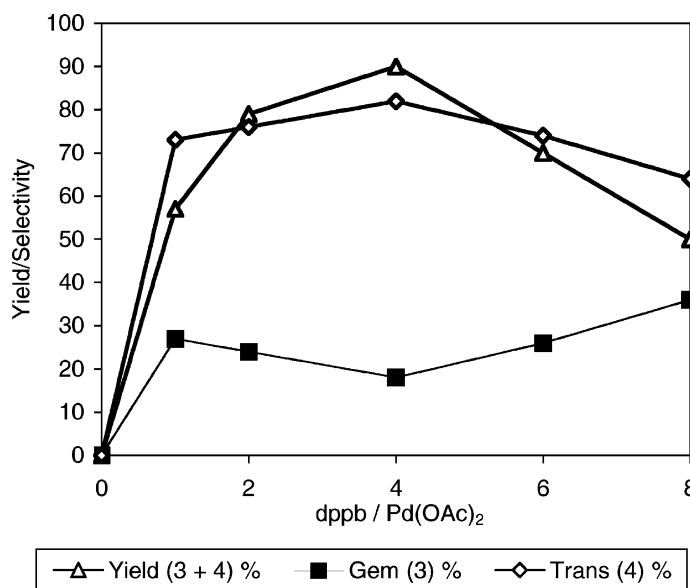
Fig. 4. Palladium(II)-catalyzed carbonylative coupling of 1-heptyne (**1a**) to aniline (**2a**). Effect of the molar ratio of dppb to Pd(OAc)$_2$ on the total yield and the selectivity of **4aa**. Reaction conditions: Pd(OAc)$_2$ (0.02 mmol), aniline and 1-heptyne (2.0 mmol), CH$_2$Cl$_2$ (10.0 ml), H$_2$ (300 psi), CO (300 psi), 110 °C, 16 h.

intermediate species in CH$_2$Cl$_2$. The good selectivity of **3aa** in a polar solvent such as THF was probably related to the solvation of the ion-pairs (palladium/counter ion), which facilitated cation–anion dissociation and therefore, rendered the metal center more electrophilic and accessible for the substrate molecules [36].

3.5. Effect of the reaction time

The effect of the reaction time on the yield and selectivity of the carbonylative coupling of aniline with 1-heptyne toward the *gem* or *trans* unsaturated amides was studied (Figs. 5 and 6). Under the conditions of the system A the full conversion and the maximum

Table 3

Palladium(II)-catalyzed carbonylative coupling of 1-heptyne (**1a**) to aniline (**2a**). Effect of solvent on the total yield and the selectivity of **3aa** and **4aa**[a]

Entry	Solvent	Ligand	Time (h)	T (°C)	CO (psi)	H$_2$ (psi)	Additive	Yield (%)[b]	Selectivity (**3aa/4aa**, %)[c]
1	THF	dppp	3	120	100	–	*p*-TsOH (0.12 mmol)	94	95/5
2	THF	dppb	16	110	300	300	–	Traces	–
3[d]	Toluene	dppp	3	120	100	–	*p*-TsOH (0.12 mmol)	89	82/18
4[e]	Toluene	dppb	16	110	300	300	–	40	48/42
5	CH$_3$CN	dppp	3	120	100	–	*p*-TsOH (0.12 mmol)	15	27/73
6	CH$_3$CN	dppb	16	110	300	300	–	3	100/0
7	CH$_2$Cl$_2$	dppp	3	120	100	–	*p*-TsOH (0.12 mmol)	31	87/13
8	CH$_2$Cl$_2$	dppb	16	110	300	300	–	90	18/82

[a] Reaction conditions: catalyst (0.02 mmol), dppp (0.04 mmol), dppb (0.08 mmol), aniline (2.0 mmol), 1-heptyne (2.0 mmol).

[b] Isolated total yield.

[c] Determined by GC and ^{1}H NMR.

[d] 10% of the cyclic compound (**5**) was formed.

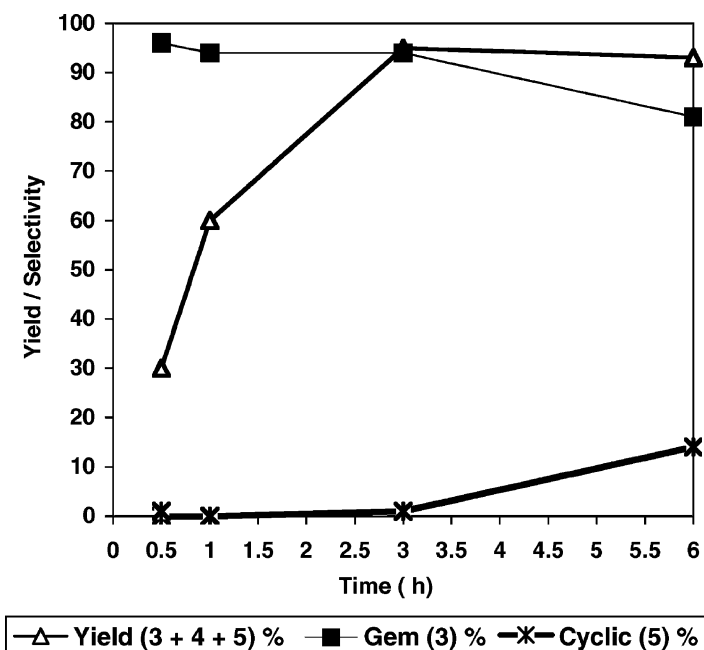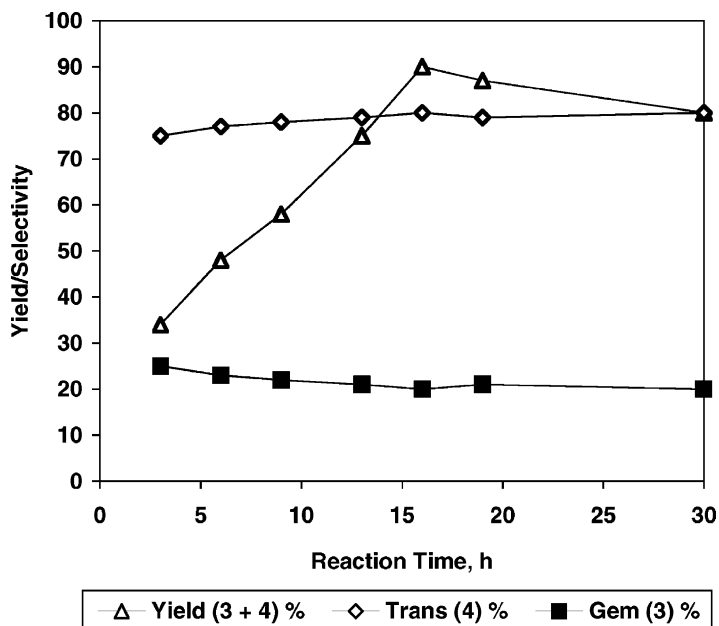[e] 20% of the cyclic compound (**5**) was formed.

Fig. 5. Palladium(II)-catalyzed carbonylative coupling of 1-heptyne (**1a**) to aniline (**2a**). Effect of the reaction time on the total yield and the selectivity of **3aa**. Reaction conditions: Pd(OAc)$_2$ (0.02 mmol), dppp (0.04 mmol), aniline (2.0 mmol), 1-heptyne (2.0 mmol), CO (100 psi), *p*-TsOH (0.12 mmol), THF (10 ml), 120 °C.

Fig. 6. Palladium(II)-catalyzed carbonylative coupling of 1-heptyne (**1a**) to aniline (**2a**). Effect of the reaction time on the total yield and the selectivity of **4aa**. Reaction conditions: Pd(OAc)$_2$ (0.02 mmol), dppb (0.04 mmol), aniline (2.0 mmol), 1-heptyne (2.0 mmol), CO (300 psi), H$_2$ (300 psi), CH$_2$Cl$_2$ (10 ml), 110 °C.

selectivity of **3aa** were obtained after 3 h of reaction. An increase in the reaction time led to the formation of the cyclic product (**5**) (Fig. 5). A slower reaction rate was observed under the conditions of the system B. The optimum reaction time was 16 h. The selectivity of the reaction toward *trans* isomer (**4aa**) remained fairly constant throughout the reaction time (Fig. 6). It seems that the active catalytic species did not evolve during the course of the reaction [37], hence the regioselectivity of the reaction is probably determined during the main catalytic cycle and depends on steric and other factors influencing the reaction mechanism [25].

3.6. Effect of the type of acid additive

The reaction of carbonylative coupling of 1-heptyne (**1a**) with aniline (**2a**) was carried out under the conditions of the system A in the presence of different acid additives (Table 4). Only traces of products were obtained in the absence of *p*-TsOH. In addition, other acid additives were also used in the reaction and the catalytic activity decreased in the following order: *p*-TsOH > CF_3CO_2H > CH_3SO_3H > *p*-nitrobenzoic acid > HCl, which represented the reverse of the coordination ability of the corresponding anion to palladium center. The highest activity was observed with *p*-TsOH (Table 4, entry 1). The presence of an anion with a strong binding ability led to less available coordination sites around the central

Table 4
Palladium(II)-catalyzed carbonylative coupling of 1-heptyne (**1a**) to aniline (**2a**). Effect of the type of acid on the total yield and the selectivity of **3aa**[a]

Entry	Acid additive	Yield (%)[b]	Selectivity (**3aa**/**4aa**, %)[c]
1[d]	*p*-TsOH	95	95/5
2	CF_3CO_2H	80	94/6
3	CH_3SO_3H	70	94/6
4	CH_3CO_2H	Traces	Traces
5	PhCOOH	Traces	Traces
6[d]	PhCOOH	91	93/7
7	*p*-NO_2–$C_6H_4CO_2H$	3	100/0
8	HCl	Traces	Traces

[a] Reaction conditions: catalyst (0.02 mmol), dppp (0.04 mmol), aniline (2.0 mmol), 1-heptyne (2.0 mmol), acid (0.12 mmol), CO (100), THF (10 ml), 120 °C, 6 h.
[b] Isolated total yield.
[c] Determined by GC and ^{1}H NMR.
[d] 24 h.

metal atom and subsequently decreased the catalytic activity of palladium [12]. In general, it was suggested that in the coordination strength of anions toward the cationic palladium(II) center is in correlation with the acid strength of the corresponding Brönsted acids. An exception to the rule comprises the halide anions, which, although derived from strong acids, strongly coordinate to palladium(II) center giving the so-called neutral palladium complexes. Therefore, that coordination ability rather than the acid/base property determined the effect of the type of the anion on the catalytic performance [38]. The higher reactivity with weakly coordinating anions is thought to arise, in part, from the ligand to the coordination sites around the metal center [39].

Also the selectivity is not affected much by the change in the concentration of *p*-TsOH, which suggested that OTs^- might not be strongly coordinated to the Pd center. The optimum molar ratio of acid to palladium was found to be six. Any further increase of this ratio did not offer any advantage [12].

3.7. Effect of the total CO pressure and CO/H_2 ratio

The effect of the CO pressure under the conditions of the system A was studied. No major change in the total yield of the unsaturated amides (**3aa** and **4aa**) and in the selectivity of **3aa** was observed at a pressure higher than 100 psi (Fig. 7).

In addition, the study of the change of the total pressure and the ratio of the partial pressure of CO and H_2 under the conditions of the system B showed that the total yields and the regioselectivity of the carbonylation reaction were seriously affected (Figs. 8 and 9). A significant improvement of the total yield from 17 to 79% was observed with the increase of the total pressure form 100 to 300 psi. The maximum yield (90%) and selectivity of **4aa** (82%) were obtained at 600 psi (Fig. 8).

The result of the effect of CO/H_2 ratio on both the rate of reaction and the composition of the isomers (**3aa** and **4aa**) were studied under the conditions of the system B (Fig. 9). Less than 10% of isolated yield of the unsaturated amides were obtained in the absence of hydrogen. Also the use of TsOH in place of hydrogen decreased the total yield to 84% and changed the selectivity of the reaction in favor of the *gem*
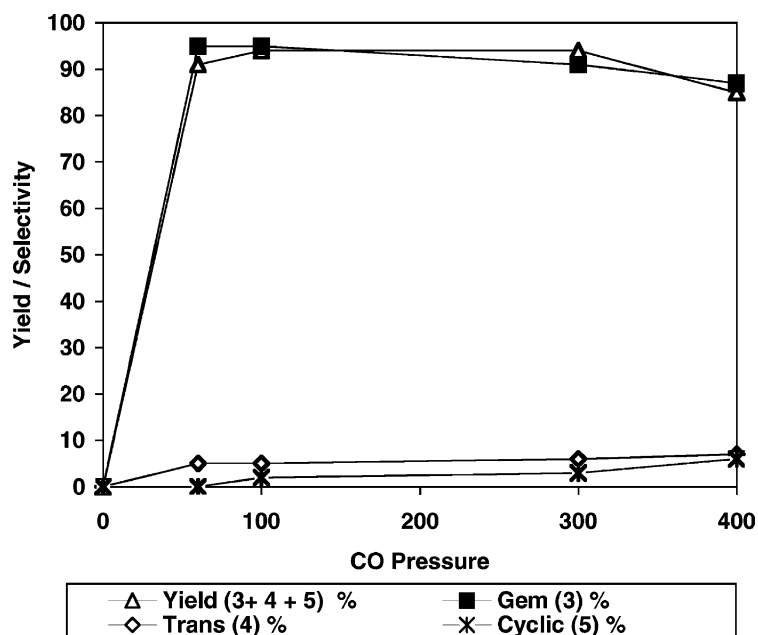
Fig. 7. Palladium(II)-catalyzed carbonylative coupling of 1-heptyne (**1a**) to aniline (**2a**). Effect of the CO pressure on the total yield and the selectivity of **3aa**. Reaction conditions: Pd(OAc)$_2$ (0.02 mmol), dppp (0.04 mmol), aniline (2.0 mmol), 1-heptyne (2.0 mmol), CO (100 psi), *p*-TsOH (0.12 mmol), THF (10 ml), 120 °C.
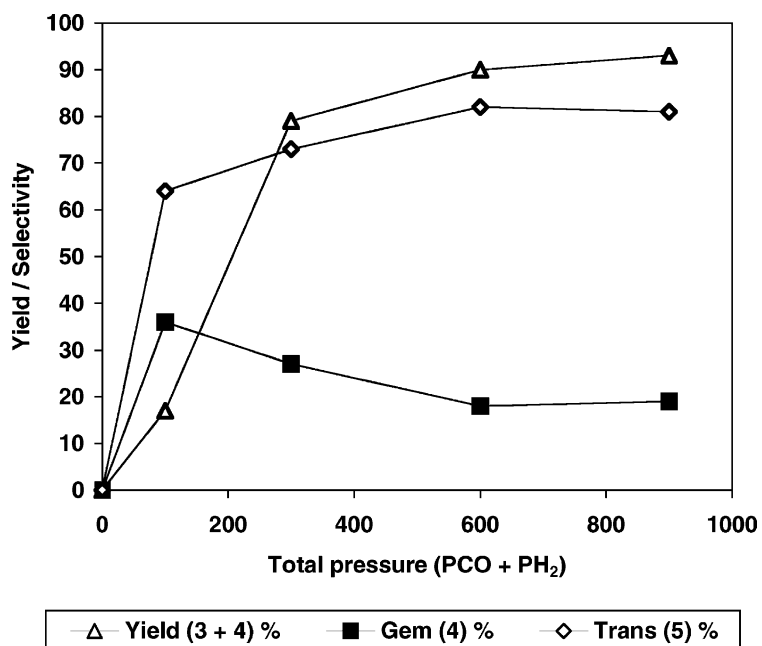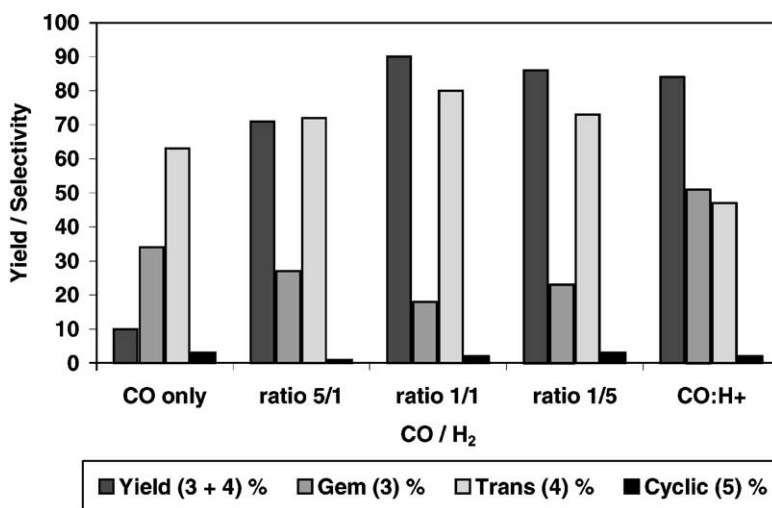

Fig. 8. Palladium(II)-catalyzed carbonylative coupling of 1-heptyne (**1a**) to aniline (**2a**). Effect of the total pressure of $CO + H_2$ on the total yield and the selectivity of **4aa**. Reaction conditions: Pd(OAc)$_2$ (0.02 mmol), dppb (0.08 mmol), aniline (2.0 mmol), 1-heptyne (2.0 mmol), CH$_2$Cl$_2$ (10.0 ml), 110 °C, 16 h.
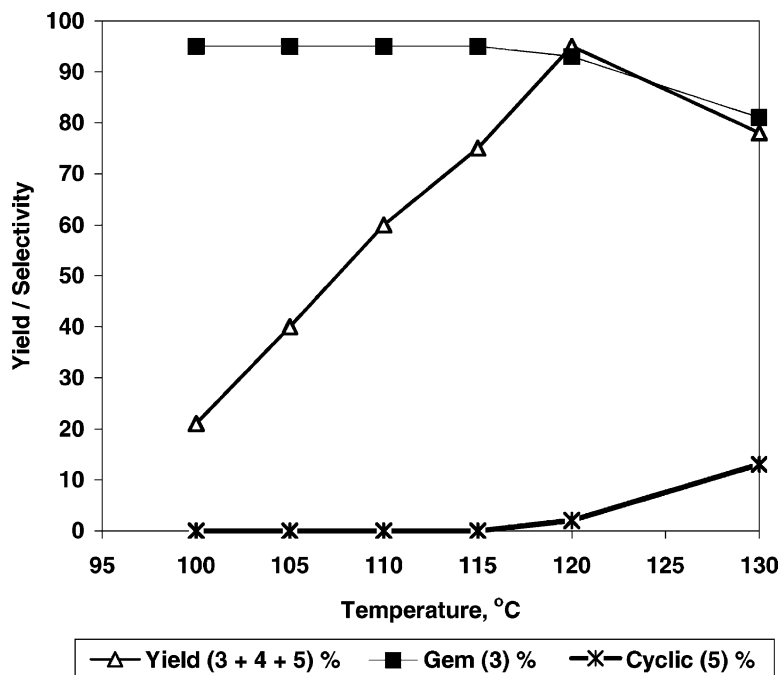
Fig. 9. Palladium(II)-catalyzed carbonylative coupling of 1-heptyne (**1a**) to aniline (**2a**). Effect of CO/H_2 ratio on the total yield and the selectivity of **4aa**. Reaction conditions: $Pd(OAc)_2$ (0.02 mmol), dppb (0.08 mmol), aniline (2.0 mmol), 1-heptyne (2.0 mmol), CH_2Cl_2 (10.0 ml), 110 °C, 16 h.

Fig. 10. Palladium(II)-catalyzed carbonylative coupling of 1-heptyne (**1a**) to aniline (**2a**). Effect of the temperature on the total yield and the selectivity of **3aa**. Reaction conditions: $Pd(OAc)_2$ (0.02 mmol), dppp (0.04 mmol), aniline (2.0 mmol), 1-heptyne (2.0 mmol), CO (100 psi), p-TsOH (0.12 mmol), THF (10 ml), 3 h.

isomer (*gem/trans*/cyclic = 51/47/2). Generally, the decrease of the ratio of CO/H_2 decreased the total yield and the selectivity. The lowest yield was obtained at CO/H_2 ratio of 5/1. At the optimum ratio of CO/H_2 of 1/1 the maximum yield (90%) and selectivity of **4aa** (82%) was obtained. The analysis of these results led us to conclude that the possible intermediate species for both mechanisms of the systems A and B were the palladium hydride. However, the occurrence of the reaction was totally different due to the effect of the type of ligand and solvent, and the most important to the use of syngas that enhanced the formation of *trans* isomer (**4aa**) as a predominant product.

3.8. Effect of temperature

The effect of the temperature was also carefully studied (Figs. 10 and 11). No reaction or traces of products were obtained under the system A at temperature below 120 °C and a very complex mixture of products at higher temperature (>120 °C). Similar results were observed under the conditions of the system B. The optimum temperature was 110 °C. Lower temperatures decrease drastically the yield of products, and higher temperatures lead to a significant amount of side products.

3.9. Carbonylative coupling of N-methyl aniline with 1-heptyne

The reaction of carbonylative coupling has been extended to secondary aryl amine, such as *N*-methyl aniline (**1b**) in the presence of 1-heptyne (**1a**). High yield (74%) and excellent selectivity (96%) of the tertiary unsaturated amide (**3ab**) were obtained under
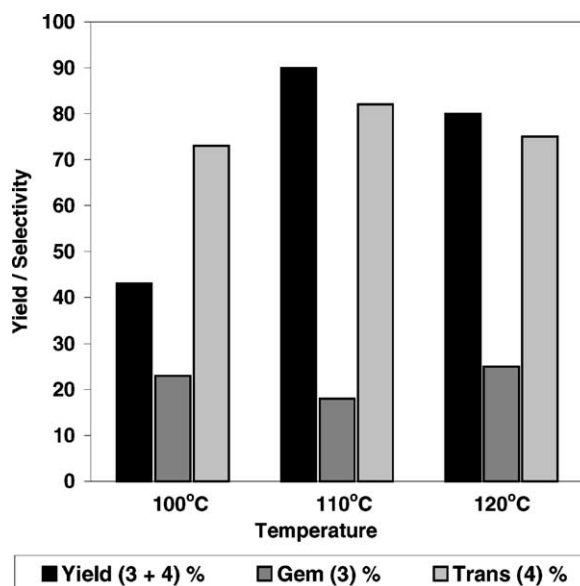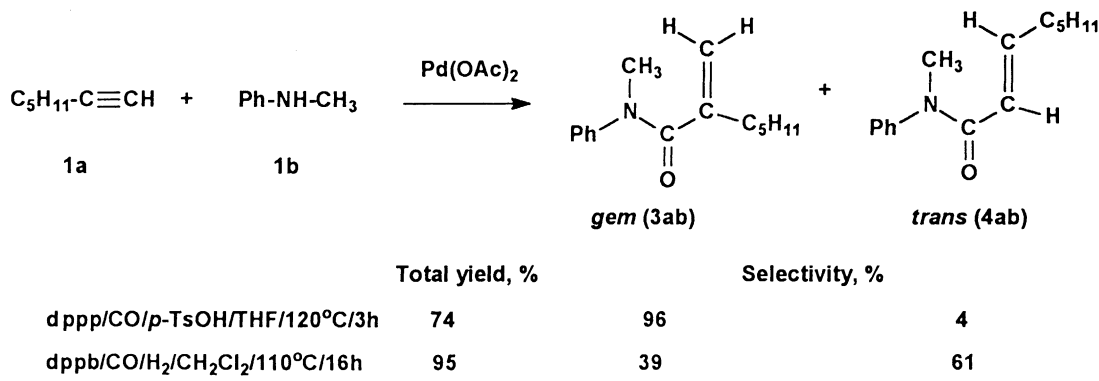

Fig. 11. Palladium(II)-catalyzed carbonylative coupling of 1-heptyne (**1a**) to aniline (**2a**). Effect of the temperature on the total yield and the selectivity of **4aa**. Reaction conditions: $Pd(OAc)_2$ (0.02 mmol), dppb (0.08 mmol), aniline (2.0 mmol), 1-heptyne (2.0 mmol), CH_2Cl_2 (10.0 ml), 110 °C, 16 h.

the experimental conditions of the system A (Eq. (2)). The total isolated yield of the tertiary unsaturated amides (**3ab** and **4ab**) was significantly improved under the conditions of the system B, but the selectivity toward the expected *trans* product (**4ab**) was lower (61%) due to the presence on the donating group methyl on the nitrogen. Both steric and electronic effects affected the regiochemistry of the reaction under the system B, but the electronic factor seems to predominate.

|	Total yield, %	Selectivity, %	
dppp/CO/*p*-TsOH/THF/120°C/3h	74	96	4
dppb/CO/H_2/CH_2Cl_2/110°C/16h	95	39	61

(2)

4. Proposed reaction schemes

The mechanisms of the reactions of the carbonylative of 1-heptyne (**1a**) with aniline (**2a**) under the conditions of system A or B are not yet well understood. Based on the analysis of the literature and the present experimental observations we tentatively propose a hydride mechanism. The catalytic activities were enhanced in the presence of H_2 or acids, such as *p*-TsOH. It was previously mentioned that the addition of acetylene to $[(Cy_3P)_2Pd(H)(HNPh)]$ [40] yielded the hydrido alkynyl complex $[(Cy_3P)Pd(H)(CCH)]$ and aniline, which indicates that the coordination of aniline was unlikely to take place at the steps of the reaction under the conditions of system A or B. In addition, when the catalytic system $Pd(OAc)_2/PPh_3/p$-TsOH was used in the hydroesterification reaction, a cationic species such as $[HPd(PPh_3)_3]^+TsO^-$ or $[Pd(COOR)(PPh_3)_3]^+TsO^-$ was isolated, characterized and proposed as the active catalytic intermediates [41].

We propose for the catalytic synthesis of *gem* unsaturated amide (**3aa**), a tentative mechanism shown on the Scheme 1 in which the neutral ligands are omitted. The hydridopalladium intermediate (**5**) may form as a key species by the reaction of $Pd(OAc)_2$ with carbon monoxide and TsOH [10,42]. Addition of the hydrido complex (**5**) to 1-heptyne may give the vinyl–palladium complex (**6**). The insertion of CO gave probably the acyl palladium intermediate

(**7**) followed by the reaction with aniline affording the α,β-unsaturated amide (**3aa**) and regenerated the active intermediate (**5**). It is possible that $Pd(OAc)_2(dppp)$ was formed at the first step followed by the reaction with TsOH to produce the active catalytic palladium hydride species HPd(dppp)OTs. It was previously suggested that tosylates, compared with acetate, seems to be preferable for the formation of such species with a smooth insertion of alkyne and CO [25,43].

The mechanism of the reaction undergoing under the system B is obviously different due to the high selectivity toward the *trans*-α,β-unsaturated amide (**4aa**) under syngas pressure (Scheme 2). We have demonstrated that the presence of the syngas was necessary for the selective synthesis of **4aa**. We propose at the first step of the reaction the formation of the palladium hydride dimer $[(dppb)PdH]_2$ (**8**) by the reaction of $Pd(OAc)_2$, dppb, CO and H_2. The coordination of alkyne to palladium center followed by the insertion of carbon monoxide may give two possible intermediates (**11** and **12**). The presence of a bulky chelating diphosphine ligand would place the group R of the alkyne away from the ligand. Therefore, the pro-linear intermediate (**11**) may be relatively more stable than the pro-branched intermediate (**12**) [44]. The migratory insertion of CO followed by the addition of PNH_2 under H_2 would form the final product (**4aa**) and regenerate the palladium dimer (**8**).
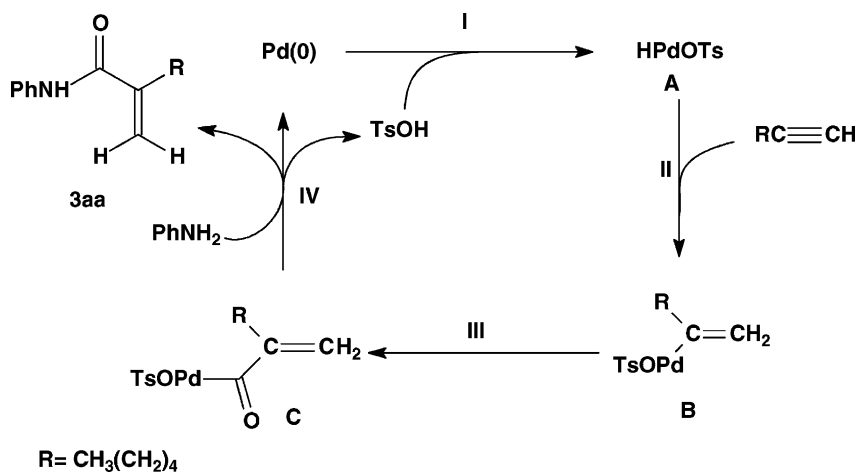
Scheme 1. Proposed mechanism for the carbonylative coupling of 1-heptyne with aniline catalyzed by Pd(OAc)₂/dppp/CO/*p*-TsOH.
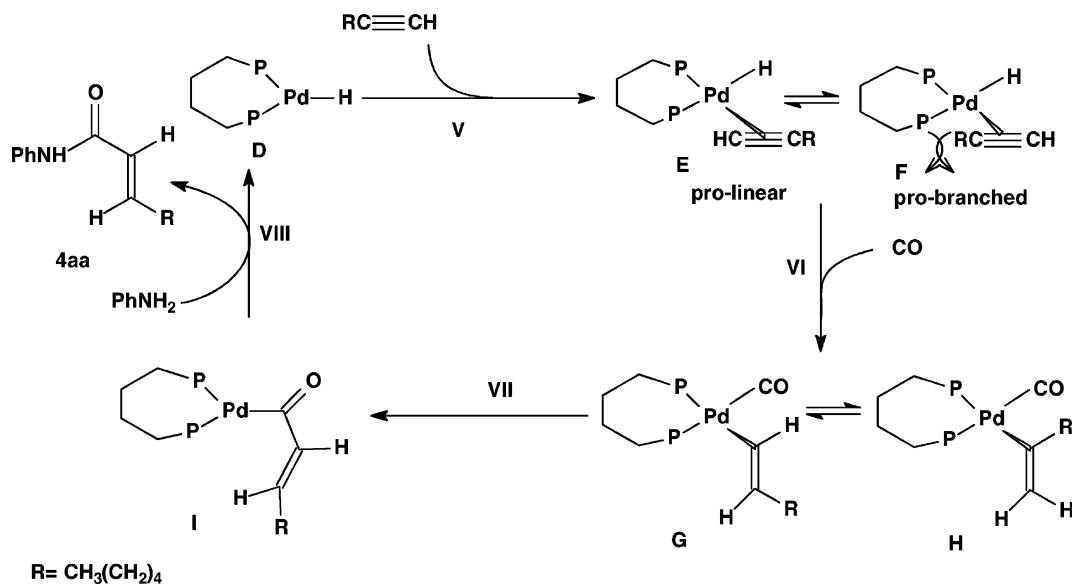
Scheme 2. Proposed mechanism for the carbonylative coupling of 1-heptyne with aniline catalyzed by Pd(OAc)$_2$/dppb/CO/H$_2$.

5. Conclusions

The regioselective carbonylative coupling of aniline to 1-heptyne was achieved successfully using either the catalytic system A [Pd(OAc)$_2$/dppp/*p*-TsOH/CO/ THF] or the system B [Pd(OAc)$_2$/dppb/CO/H$_2$/CH$_2$-Cl$_2$]. The system A provided an efficient and simple method for the synthesis of new *gem*-α,β-unsaturated amide (**3aa**). The other catalytic system B represented an attractive new route for the production of *trans*-α,β-unsaturated amide (**4aa**), which was difficult to obtain otherwise. These methods demonstrated the high efficiency of palladium acetate associated to dppb or dppp as an active catalyst of carbonylation reaction in the synthesis of highly useful compounds, such as α,β-unsaturated amides. The regioselectivity of the carbonylative coupling was very sensitive to the type additive and to the use of syngas. The *N*-methyl aniline with 1-heptyne gave also excellent yields and selectivity of the tertiary *gem*- and *trans*-α,β-unsaturated amides. Currently, we are examining the carbonylative coupling of various aniline derivatives with different alkyl alkynes using the catalytic systems A and B. The carbonylative coupling of primary and secondary alkylamines and diamines with terminal, internal alkyl and aromatic alkynes are also considered in the next phase.

Acknowledgements

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