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Catalytic and regioselective synthesis of gem- or trans-α,β-unsaturated amides by carbonylation of alkyl alkynes with aniline derivatives by palladium(II) and phosphine

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The reaction of carbonylative addition of alkyl alkynes to aniline derivatives has been successfully achieved by a catalytic system formed of $Pd(OAc)_2$ and a suitable bidentate phosphine ligand. The reaction led mainly to gem-α,β-unsaturated amides (3) with $Pd(OAc)_2$/1,3-bis(diphenylphosphino)propane/*p*-toluenesulfonic acid/CO as the catalytic system. However, the reaction catalyzed by $Pd(OAc)_2$/1,4-bis(diphenylphosphino)butane/H_2/CO in CH_2Cl_2 as a solvent affords trans-α,β-unsaturated amides (4) as the major product. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: carbonylative addition; alkynes; aniline; palladium; dppb; syngas; unsaturated amides

INTRODUCTION

The synthesis of saturated and unsaturated amides is an important area of organic chemistry at the industrial and academic levels.[1] In the last decade, the production of various carbonyl compounds catalyzed by various transition-metal complexes has represented an important and new route in fine chemistry.[2,3] Previously, the synthesis of *N*-aryl acrylamides was achieved by the reaction of aromatic amines with 2-substituted acryloyl chlorides or substituted acrylic acid.[4] The 2-substituted acrylamides are important intermediates for the synthesis of polymers.[5] The direct synthesis of 2-substituted acrylamides from alkynes and amines has previously been reported using various transition-metal complexes.[6–11]

Active soluble palladium complexes are among the most widely used in selective carbonylation chemistry. For example, branched and linear α,β-unsaturated acids and their derivatives are produced by the palladium-catalyzed carbonylation of alkynes.[12] The regioselectivity depends strongly on the catalytic system and the reaction conditions.[12] Branched α,β-unsaturated acids or esters are produced as the main products by using the catalytic systems formed of palladium black/HI,[13] Palladium(II) dibenzalacetone [$Pd(dba)_2$]/1,4-bis(diphenylphosphine)butane (dppb),[14] $Pd(PPh_3)_4$/dppf,[15,16] $Pd(dba)_2$/PPh_3/*p*-toluenesulfonic acid (*p*-TsOH),[17–21] $Pd(OAc)_2$/dppb/PPh_3/*p*-TsOH,[22] $Pd(OAc)_2$/2-pyridyldiphenylphosphine/$MeSO_3H$ or $Pd(OAc)_2$/tri(2-furyl)phosphine/$MeSO_3H$.[23] Only a few reports on palladium complexes as catalysts that can selectively lead to linear unsaturated acid derivatives as the major products have been reported.[24,25] Recently, we have described a new and efficient method for the selective production of gem- or trans-α,β-unsaturated amides, esters and thiols.[26–28]

In this paper we report the results of the carbonylative addition of aniline derivatives to various alkyl alkynes producing various new and substituted gem- and trans-α,β-unsaturated amides. The reaction conditions and the catalyst system have a great effect in the inversion of the regioselectivity of the reaction.

EXPERIMENTAL

General

Aniline derivatives, alkynes, palladium complexes, phosphine ligands, and carboxylic acids are commercially available materials and were used without any further purification.

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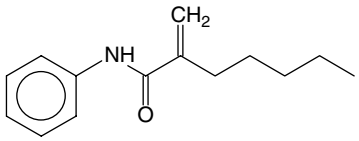
Contract/grant sponsor: King Fahd University of Petroleum and Minerals.

Dry and freshly distilled solvents have been used in all experiments. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 500 MHz Joel l500 NMR machine. IR spectra were recorded on a Perkin Elmer 16F PC FT-TR spectrometer and are reported in wavenumbers (cm^{-1}). Gas chromatography (GC) analyses were realized on HP 6890 plus chromatography.

General procedure for the carbonylative coupling of terminal alkyl alkynes with anilines derivatives

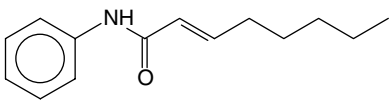
$Pd(OAc)_2$ (0.02 mmol), 1,3-bis(diphenylphosphino)propane (dppp; 0.04 mmol) or dppb (0.08 mmol), *p*-TsOH (0.12 mmol if used), alkynes (2.0 mmol), aniline derivative (2.0 mmol), and 10 ml of solvent were added into a 45 ml Parr autoclave fitted with a glass liner containing a stirring bar. The autoclave was vented three times with CO and then pressurized at room temperature with 100 psi CO only (or pressurized with 300 psi CO and 300 psi H_2 in the other system). 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 thin-layer chromatography (petroleum ether : acetone 10 : 1). The products were identified by ^{1}H and ^{13}C NMR, fourier transform infrared (FT-IR), GC–mass spectrometry (MS) and elemental analysis. The spectra and analytical data for the α,β-unsaturated amides synthesized are given below.

N-Phenyl-2-pentyl-propeneamide (3)



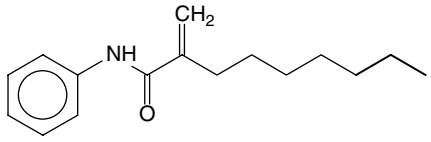
White crystals, m.p. 60 °C. IR (KBr) ν (cm^{-1}): 16.56 (CO). ^{1}H NMR δ (ppm) $CDCl_3$: 0.90 (t, 3H, $J = 6.7$ Hz, CH_3), 1.31 (m, 4H, $(CH_2)_2CH_3$), 1.59 (m, 2H, $CH_2CH_2CH_2$), 2.38 (t, 2H, $J = 7.9$ Hz, C=CH_2), 5.36 (s, 1H, CH_2), 5.68 (s, 1H, C=CH_2), 7.08–7.58 (m, 5H, C_6H_5), 7.74 (s, 1H, N*H*). ^{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). MS: m/z 217 (M^+). Anal. Found: C, 77.51; H, 8.63; N, 6.49. Calc. for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45%.

(*E*)-*N*-Phenyl-2-octeneamide (4)



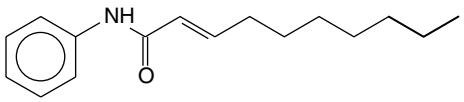
White crystals, m.p. 76 °C. IR (KBr) ν (cm^{-1}): 1666 (CO). ^{1}H NMR δ (ppm) $CDCl_3$: 0.90 (t, 3H, $J = 6.7$ Hz, CH_3), 1.31 (m, 4H, CH_2CH_3), 1.71 (m, 4H, $CH_2(CH_2)_2CH_2$), 2.12 (q, =$CHCH_2$), 5.91–5.94 (d, 1H, CH=C*H*–CO, $J = 15.25$ Hz), 6.92–6.95 (m, 1H, C*H*=CH–CO), 7.09–7.70 (m, 5H + 1H, C_6H_5 + N*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). MS: m/z 217 (M^+). Anal. Found: C, 77.31; H, 8.93; N, 6.47. Calc. for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45%.

N-Phenyl-2-heptyl-propeneamide (5)



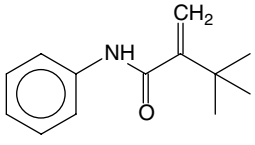
White crystals, m.p. 63 °C. IR (KBr) ν (cm^{-1}): 1656 (CO). ^{1}H NMR δ (ppm) $CDCl_3$: 0.78 (t, 3H, $J = 6.7$ Hz, CH_3), 1.16–1.19 (m, 8H, $CH_2(CH_2)_4CH_3$), 1.36 (m, 2H, =CCH_2CH_2), 2.84 (t, 2H, $J = 7.9$ Hz, C=CH_2), 5.36 (s, 1H, C=CH_2), 5.68 (s, 1H, C=CH_2), 7.08–7.58(m, 5H, C_6H_5), 7.74 (s, 1H, N*H*). ^{13}C NMR δ (ppm) $CDCl_3$: 13.73, 21.94, 22.52, 22.66, 27.74, 31.52, 32.62, 117.43, 119.90, 124.18, 129.05, 138.02, 146.63, 167.55. MS: m/z 245 (M^+). Anal. Found: C, 78.10; H, 9.61; N, 5.59. Calc. for $C_{16}H_{23}NO$: C, 78.32; H, 9.45; N, 5.71%.

(*E*)-*N*-Phenyl-2-deceneamide (6)



White crystals, m.p. 79 °C. IR (KBr) ν (cm^{-1}): 1660 (CO). ^{1}H NMR δ (ppm) $CDCl_3$: 0.86 (t, 3H, $J = 6.7$ Hz, CH_3), 1.31 (m, 4H, $CH_2(CH_2)_2CH_3$), 1.70–192 (m, 6H, $-(CH_2)_3-$), 2.22 (q, 2H, =$CHCH_2$), 5.91–5.94 (d, 1H, $J = 15.20$ Hz, –CH=C*H*–CO), 6.92–6.95 (m, 1H, –C*H*=CH–CO), 7.09–7.70 (m, 5H + 1H, C_6H_5 + N*H*). ^{13}C NMR δ (ppm) $CDCl_3$: 13.90, 21.92, 22.36, 22.41, 26.15, 27.64, 31.09, 31.43, 31.85, 34.56, 121.25, 123.59, 128.89, 13.95, 146.60, 164.65. MS: m/z 245 (M^+). Anal. Found: C, 78.54; H, 9.32; N, 5.88. Calc. for $C_{16}H_{23}NO$: C, 78.32; H, 9.45; N, 5.71%.

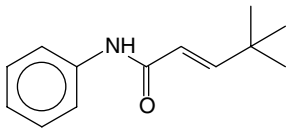
N-Phenyl-2-t-butyl propeneamide (7)



White crystals, m.p. 125 °C. IR (KBr) ν (cm^{-1}): 1656 (CO). ^{1}H NMR δ (ppm) $CDCl_3$: 1.12 (s, 9H, $C(CH_3)_3$), 5.42 (s, 1H, =CH_2), 5.74 (s, 1H, =CH_2), 6.98–7.56 (m, 5H + 1H, C_5H_5 + N*H*). ^{13}C NMR δ (ppm) $CDCl_3$: 29.32, 35.39, 113.39, 119.85, 124.33, 128.99, 137.9, 156.72, 168.18 (CO). MS: m/z

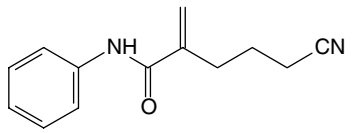
203 (M^+). Anal. Found: C, 76.91; H, 8.25; N, 6.79. Calc. for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89%.

(*E*)-*N*-Phenyl-4,4-dimethyl-2-buteneamide (8)



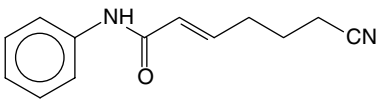
White crystals, m.p. 170 °C. IR (KBr) ν (cm^{-1}): 1668 (CO). ^{1}H NMR, δ (ppm) $CDCl_3$: 1.11 (s, 9H, $C(CH_3)_3$), 5.81–5.84 (d, 1H, $J = 15.25$ Hz, –CH=C*H*–CO), 6.98–7.01 (d, 1H, $J = 15.25$ Hz, –C*H*=CH–CO), 7.09–7.56 (m, 5H + 1H, $C_6H_5 + NH$). ^{13}C NMR δ (ppm) $CDCl_3$: 28.83, 33.67, 119.85, 124.21, 129.00, 156.37, 164.54 (CO). MS: m/z 203 (M^+). Anal. Found: C, 76.96; H, 8.55; N, 6.74. Calc. for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89%.

N-Phenyl-3-propylnitrile-2-propeneamide (9)



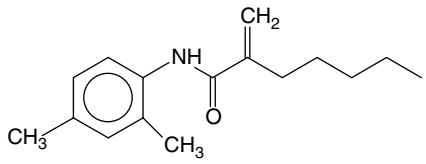
Oil. IR (KBr) ν (cm^{-1}): 1683 (CO). ^{1}H NMR δ (ppm) $CDCl_3$: 1.18 (m, 2H, $CH_2CH_2CH_2$), 2.37 (t, 2H, $J = 8.05$ Hz, CH_2CH_2CN), 2.54 (t, 2H, $J = 7.15$ Hz, C=CH_2), 5.59 (s, 1H, C=CH_2), 5.75 (s, 1H, C=CH_2), 7.11–7.56 (m, 5H, C_5H_5), 7.86 (s, br, 1H, N*H*). ^{13}C NMR δ (ppm) $CDCl_3$: 16.50, 23.86, 31.56, 119.2, 119.25, 119.46, 120.15, 124.49, 128.88, 137.56, 144.08, 166.37 (CO). MS: m/z 242 (M^+). Anal. Found: C, 72.62; H, 6.41; N, 13.02. Calc. for $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.07%.

(*E*)-*N*-Phenyl-6-cyano-2-penteneamide (10)



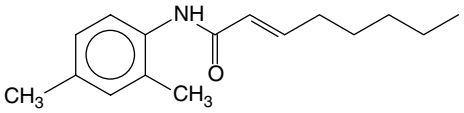
Oil. IR (KBr) ν (cm^{-1}): 1675 (CO). ^{1}H NMR δ (ppm) $CDCl_3$: 1.28 (m, 2H, $CH_2CH_2CH_2$), 1.73 (t, 2H, $J = 7.08$ Hz, CH_2CN), 2.30 (m, 2H, $CNCH_2CH_2$), 2.60 (m, 2H, CH=CHCH_2), 6.05–6.08 (d, 1H, $J = 15.55$ Hz, CO–C*H*=CH–), 6.83 (m, 1H, COCH=C*H*–), 7.08–7.61 (m, 5H, C_6H_5–), 8.36 (1H, –N*H*, br). ^{13}C NMR δ (ppm) $CDCl_3$: 16.31, 23.66, 30.39, 119.19, 120.09, 124.20, 125.88, 128.75, 128.83, 163.88. MS: m/z 214 (M^+). Anal. Found: C, 72.72; H, 6.51; N, 13.12. Calc. for $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.07%.

N-(2,4-Dimethylphenyl)-2-pentyl-propeneamide (11)



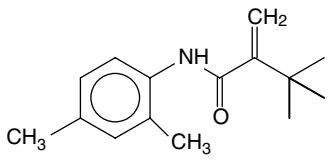
White crystals, m.p. 67 °C. IR (KBr) ν (cm^{-1}): 1660 (CO). ^{1}H NMR δ (ppm) $CDCl_3$: 0.90 (t, 3H, $J = 7.35$ Hz, CH_3), 1.34 (m, 4H, $CH_3(CH_2)_2$), 1.51 (m, 2H, $CH_2CH_2CH_2$), 2.23 (s, 3H, $C_6H_3CH_3$), 2.29 (s, 3H, $C_6H_3CH_3$), 2.40 (t, 2H, $J = 7.55$ Hz, =CCH_2), 5.34 (s, 1H, =CH_2), 5.71 (s, 1H, =CH_2), 7.00–7.70 (m, 3H + 1H, C_6H_3 + N*H*). ^{13}C NMR δ (ppm) $CDCl_3$: 13.39, 17.66, 20.83, 22.43, 27.83, 31.43, 32.52, 117.46, 123.13, 127.29, 129.13, 131.07, 132.97, 134.87, 146.53, 167.00. MS: m/z 251 (M^+). Anal. Found: C, 78.13; H, 9.66; N, 5.76. Calc. for $C_{16}H_{23}NO$: C, 78.32; H, 9.45; N, 5.71%.

(*E*)-*N*-(2,4-Dimethylphenyl)-2-octeneamide (12)



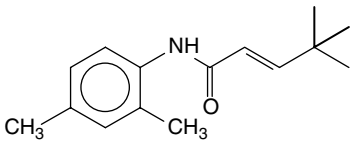
White crystals, m.p. 117 °C. IR (KBr) ν (cm^{-1}): 1666 (CO). ^{1}H NMR δ (ppm) $CDCl_3$, 0.89 (t, 3H, $J = 9.5$ Hz, CH_3), 1.30 [m, 4H, $CH_3(CH_2)_3$], 1.52 (m, 2H, $CH_2CH_2CH_2$), 2.23 (s, 3H, $C_6H_3CH_3$), 2.29 (s, 3H, $C_6H_3CH_3$), 5.95–5.98 (d, 1H, $J = 15.25$ Hz, CO–C*H*=CH), 6.95–7.26 (m, 4H, C*H*=CHCO + C_6H_3), 7.71 (s, br, N*H*). ^{13}C NMR δ (ppm) $CDCl_3$: 13.96, 17.74, 20.86, 22.43, 27.89, 31.35, 32.10, 123.27, 127.28, 131.09, 133.09, 146.22, 154.62, 164.56. MS: m/z 251 (M^+). Anal. Found: C, 78.51; H, 9.38; N, 5.65. Calc. for $C_{16}H_{23}NO$: C, 78.32; H, 9.45; N, 5.71%.

N-(2,4-Dimethylphenyl)-2-t-butyl-propeneamide (13)



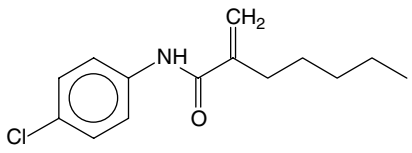
White crystals, m.p. 132 °C. IR (KBr) ν (cm^{-1}): 1659 (CO). ^{1}H NMR δ (ppm) $CDCl_3$: 1.12 (s, 9H, $C(CH_3)_3$), 2.28 (s, 3H, $C_6H_3CH_3$), 2.32 (s, 3H, $C_6H_3CH_3$), 5.42 (s, 1H, =CH_2), 5.74 (s, 1H, =CH_2), 6.98–7.56 (m, 5H + 1H, C_5H_5 + N*H*). ^{13}C NMR δ (ppm) $CDCl_3$: 29.50, 35.65, 113.55, 120.10, 125.06, 129.60, 130.98, 133.21, 137.9, 157.02, 169.08 (CO). MS: m/z 231 (M^+). Anal. Found: C, 78.02; H, 9.36; N, 5.92. Calc. for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05%.

(*E*)-*N*-(2,4-Dimethylphenyl)-4,4-dimethyl-2-penteneamide (14)



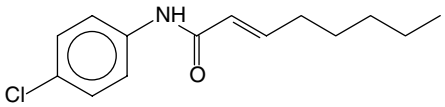
White crystals, m.p. 173 °C. IR (KBr) ν (cm^{-1}): 1662 (CO). ^{1}H NMR δ (ppm) $CDCl_3$: 1.12 (s, 9H, C(CH_3)$_3$), 2.26 (s, 3H, $C_6H_3CH_3$), 2.30 (s, 3H, $C_6H_3CH_3$), 5.90–5.95 (d, 1H, J = 15.20 Hz, CO–C*H*=CH), 6.95–7.26 (m, 4H, C*H*=CHCO + C_6H_3), 7.71 (s, br, N*H*). ^{13}C NMR δ (ppm) $CDCl_3$: 28.65, 33.42, 34.48, 120.13, 128.93, 131.26, 132.90, 145.98, 155.95, 165.03. MS: m/z 231 (M^+). Anal. Found: C, 77.92; H, 9.43; N, 6.19. Calc. for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05%.

N-(4-Chlorophenyl)-2-pentyl-propeneamide (15)



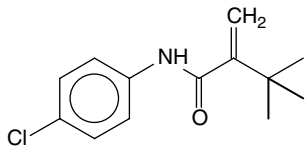
White crystals, m.p. 69 °C. IR (KBr) ν (cm^{-1}): 1660 (CO). ^{1}H NMR δ (ppm) $CDCl_3$: 0.89 (t, 3H, J = 6.6 Hz, CH_3), 1.33 (m, 4H, (CH_2)$_2$$CH_3$), 1.50 (m, 2H, $CH_2CH_2CH_2$), 2.38 (t, 2H, J = 7.85 Hz, =CCH_2), 5.40 (s, 1H, C=CH_2), 5.70 (s, 1H, C=CH_2), 7.26–7.53 (m, 4H, C_6H_4), 7.58 (s, br, –N*H*). ^{13}C NMR δ (ppm) $CDCl_3$: 13.97, 22.41, 27.80, 31.42, 32.33, 117.91, 121.16, 128.99, 129.31, 136.41, 146.29, 167.01 (CO). MS: m/z 251 (M^+). Anal. Found: C, 66.93; H, 7.41; N, 5.43. Calc. for $C_{14}H_{18}ClNO$: C, 66.79; H, 7.21; N, 5.56%.

(*E*)-*N*-(4-Chlorophenyl)-2-octeneamide (16)



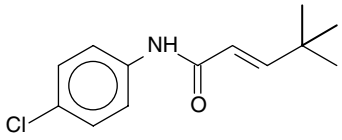
White crystals, m.p. 114 °C. IR (KBr) ν (cm^{-1}): 1677 (CO). ^{1}H NMR δ (ppm) $CDCl_3$: 0.87 (t, 3H, J = 16.95 Hz, CH_3), 1.26 (m, 4H, (CH_2)$_2$$CH_3$), 1.37 (m, 2H, $CH_2CH_2CH_2$), 2.12 (m, 2H, CH_2CH=), 6.01–6.04 (d, 1H, J = 15.25 Hz, CH=C*H*–CO), 6.92–6.95 (m, 1H, C*H*=CHCO), 6.92–8.64 (m, 4H + 1H, C_6H_4– + N*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). MS: m/z 251, (M^+). Anal. Found: C, 66.86; H, 7.46; N, 5.47. Calc. for $C_{14}H_{18}ClNO$: C, 66.79; H, 7.21; N, 5.56%.

N-(4-Chlorophenyl)-2-t-butyl-propeneamide (17)



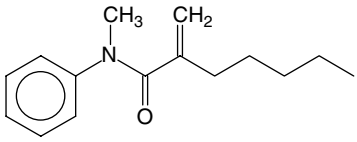
White crystals, m.p. 124 °C. IR (KBr) ν (cm^{-1}): 1661 (CO). ^{1}H NMR δ (ppm) $CDCl_3$: 1.12 (s, 9H, C(CH_3)$_3$), 5.42 (s, 1H, =CH_2), 5.74 (s, 1H, =CH_2), 6.98–7.56 (m, 4H + 1H, C_6H_5 + N*H*). ^{13}C NMR δ (ppm) $CDCl_3$: 29.50, 35.65, 113.55, 120.10, 125.06, 129.60, 133.21, 137.9, 157.02, 169.08 (CO). MS: m/z 237 (M^+). Anal. Found: C, 66.01; H, 6.62; N, 5.76. Calc. for $C_{13}H_{16}ClNO$: C, 65.68; H, 6.78; N, 5.89%.

N-(4-Chlorophenyl)-2,4-dimethyl-2-penteneamide (18)



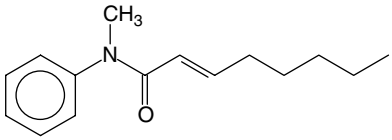
White crystals, m.p. 164 °C. IR (KBr) ν (cm^{-1}): 1658 (CO). ^{1}H NMR δ (ppm) $CDCl_3$: 1.14 (s, 9H, C(CH_3)$_3$), 2.31 (s, 3H, $C_6H_3CH_3$), 2.35 (s, 3H, $C_6H_3CH_3$), 5.85–5.98 (d, 1H, J = 15.20 Hz, CO–C*H*=CH), 6.90–7.30 (m, 5H, C*H*=CHCO + C_6H_4), 7.71 (s, br, N*H*). ^{13}C NMR δ (ppm) $CDCl_3$: 28.65, 33.42, 34.48, 120.13, 128.93, 145.98, 155.95, 165.03. MS: m/z 237 (M^+). Anal. Found: C, 65.32; H, 6.96; N, 6.12. Calc. for $C_{13}H_{16}ClNO$: C, 65.68; H, 6.78; N, 5.89%.

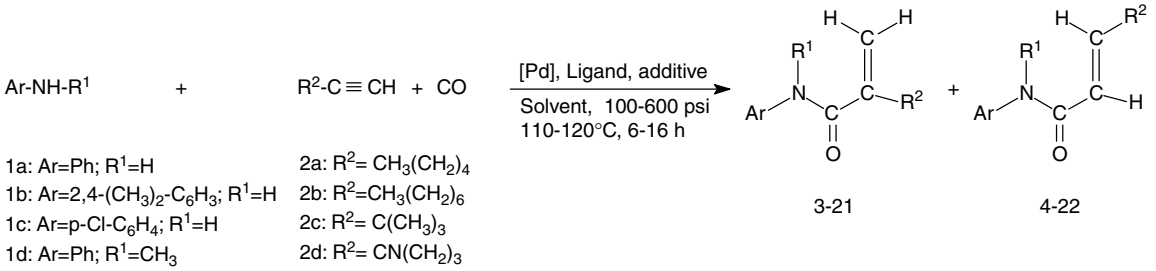
N,N-Methylphenyl-2-pentyl-propeneamide (19)



White crystals, m.p. 79 °C. IR (KBr) ν (cm^{-1}): 1640 (CO). ^{1}H NMR δ (ppm) $CDCl_3$: 0.86 (t, 3H, J = 7.3 Hz, –CH_3), 1.17–1.40 (m, 6H CH_3(CH_2)$_3$), 2.05 (t, 3H, J = 7.95 Hz, =CCH_2), 3.35 (s, 3H, N–CH_3), 5.03 (s, 2H, =CCH_2), 7.13–7.35 (m, 5H, C_5H_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). MS: m/z 231 (M^+). Anal. Found: C, 77.95; H, 9.35; N, 6.19. Calc. for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05%.

N,N-Methylphenyl-2-octeneamide (20)

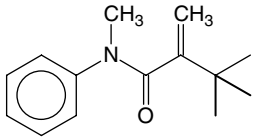




Scheme 1.

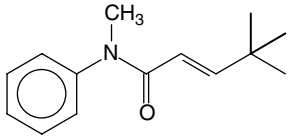
White crystals, m.p. 86 °C. IR (KBr) ν(cm^{-1}): 1650 (CO). ^{1}H NMR δ (ppm) $CDCl_3$: 0.76 (t, 3H, $J = 7.05$ Hz, CH_3CH_2), 1.16 (m, 4H, $CH_2CH_2CH_3$), 1.24 (m, 2H, $CH_2CH_2CH_2$), 1.94 (t, 2H, $J = 7.95$ Hz, $CHCH_2$), 3.24 (s, 3H, NCH_3), 5.62 (d, 1H, $J = 15.25$ Hz, CH=CH), 6.81 (m, 1H, CH=CH), 7.04–7.32 (m, 5H, C_6H_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. MS: m/z 231 (M^+). Anal. Found: C, 77.65; H, 9.22; N, 6.25. Calc. for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05%.

N,N-Methylphenyl-2-t-butyl-propeneamide (21)



White crystals, m.p. 136 °C. IR (KBr) ν(cm^{-1}): 1665 (CO). ^{1}H NMR δ (ppm) $CDCl_3$: 1.15 (s, 9H, $C(CH_3)_3$), 3.35 (s, 3H, NCH_3), 5.39 (s, 1H, =CH_2), 5.69 (s, 1H, =CH_2), 6.88–7.62 (m, 5H, C_6H_5). ^{13}C NMR δ (ppm) $CDCl_3$: 28.95, 34.88, 112.95, 121.05, 124.83, 130.52, 132.79, 136.8, 169.85 (CO). MS: m/z 217 (M^+). Anal. Found: C, 77.43; H, 9.06; N, 6.89. Calc. for $C_{14}H_{19}NO$: C, 77.38; H, 8. 81; N, 6.45%.

N-2,4-Trimethyl-*N*-phenyl-2-penteneamide (22)



White crystals, m.p. 177 °C. IR (KBr) ν(cm^{-1}): 1658 (CO). ^{1}H NMR δ (ppm) $CDCl_3$: 1.17 (s, 9H, $C(CH_3)_3$), 3.39 (s, 3H, NCH_3), 5.88–5.90 (d, 1H, $J = 15.20$ Hz, CO–CH=CH), 6.92–7.42 (m, 6H, CH=CHCO + C_6H_5). ^{13}C NMR δ (ppm) $CDCl_3$: 28.98, 32.96, 34.78, 119.76, 129.11, 146.05, 166.20. MS: m/z 217 (M^+). Anal. Found: C, 77.65; H, 8.56; N, 6.59. Calc. for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45%.

RESULTS AND DISCUSSION

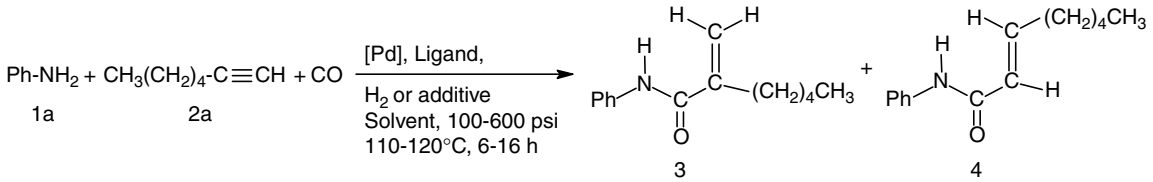
The synthesis of α,β-unsaturated amides was performed by the direct carbonylative addition of aniline derivatives **1a–d** to terminal alkyl alkynes **2a–d** in the presence of CO/*p*-TsOH/THF or CO/H_2/CH_2Cl_2 (Scheme 1). Palladium complex, phosphine ligand, and acid as additive (if used) were added separately to the solvent. The catalytic active species was generated *in situ*. The control of the regioselectivity was described previously by the detailed study of the carbonylative addition of aniline (**1a**) and 1-heptyne (**2a**) used as model substrates.[28]

Effect of the type of palladium complex

The effect of the type of palladium complex on the control of the regioselectivity of the reaction of the carbonylative addition of 1-heptyne to aniline has been studied in detail.[28] The results obtained showed clearly that different catalytic systems gave totally different regioselectivity of the reaction. A summary of the results on the effect of type of palladium complex is given in Table 1. It was interesting to observe that $Pd(OAc)_2$ was the most active catalyst in controlling the regioselectivity of the reaction compared with $PdCl_2$, $PdCl_2(PPh_3)_2$, Pd/C, and $Pd(PPh_3)_4$ (Table 1, entries 1–10). However, the catalytic system consisting of $Pd(OAc)_2$/dppp/*p*-TsOH/CO in THF as a solvent at 120 °C and 6 h successfully catalyzed the reaction of carbonylative addition of 1-heptyne (**2a**) to aniline (**1a**) to produce selectively the gem-α,β-unsaturated amide (**3**) with excellent isolated yield (94%) and selectivity (95%) (Table 1, entry 1). However, the use of the catalytic system formed of $Pd(OAc)_2$/dppb/CO/H_2 in CH_2Cl_2 at 110 °C and 16 h produced selectively the trans-α,β-unsaturated amide (**4**) (total yield: 90%; selectivity: 82% Table 1, entry 2).

In order to understand the mechanism of the reaction, the complex $Pd(OTs)_2$(dppp) has been synthesized and used in the reaction. $Pd(OTs)_2$(dppp) with no additional dppp and *p*-TsOH gave a low yield (40%) of the unsaturated amides but the high selectivity toward **3** was maintained (94%) (Table 1, entry 11). Interestingly, the addition of 0.12 mmol of *p*-TsOH to the previous experiment involving $Pd(OTs)_2$(dppp) as a catalyst increased the yield (>90%) of products significantly and the selectivity toward **3** was also kept high (95%). These

Table 1. Palladium-catalyzed carbonylative coupling of aniline (**1a**) to 1-heptyne (**2a**).[a] Effect of the type of palladium catalyst on the total yield and the selectivity[24]



Entry	Catalyst	Ligand/amount (mmol)	Time (h)/ T(°C)	CO (psi)	Additive or H_2 (psi)/solvent	Yield[b] (%)	Product distribution[c] (%) **3**	**4**
1	$Pd(OAc)_2$	dppp/0.04	6/120	100	*p*-TsOH/THF	94	95	5
2		dppb/0.08	16/110	300	H_2(300)/CH_2Cl_2	90	18	82
3	$PdCl_2$	dppp/0.04	6/120	100	*p*-TsOH/THF	13	100	0
4		dppb/0.08	16/110	300	H_2(300)/CH_2Cl_2	57	26	74
5	$PdCl_2(PPh_3)_2$	dppp/0.04	6/120	100	*p*-TsOH/THF	23	100	0
6		dppb/0.08	16/110	300	H_2(300)/CH_2Cl_2	64	26	74
7	Pd/C (10%)	dppp/0.04	6/120	100	*p*-TsOH/THF	31	100	0
8		dppb/0.08	16/110	300	H_2(300)/CH_2Cl_2	61	24	76
9	$Pd(PPh_3)_4$	dppp/0.04	6/120	100	*p*-TsOH/THF	50	95	5
10		dppb/0.08	16/110	300	H_2(300)/CH_2Cl_2	80	28	72
11	$Pd(OAc)_2$(dppp)	dppp/0.04	6/120	100	*p*-TsOH/THF	95	94	6
12[d]	$Pd(OAc)_2$(dppb)	dppb/0.08	16/110	300	H_2(300)/CH_2Cl_2	41	42	58

[a] Reaction conditions: catalyst (0.02 mmol), aniline (2.0 mmol), 1-heptyne (2.0 mmol), *p*-TsOH (0.12 mmol), THF (10 ml).
[b] Isolated total yield.
[c] Determined by GC and ^{1}H NMR.
[d] No ligand was added.

results explain the essential role of the acid *p*-TsOH in the formation and the stabilization of a possible cationic palladium hydride [(dpppPdH)$^{+-}$OTs] as an intermediate. On the other hand, the complex $Pd(OAc)_2$(dppb) was also synthesized and used in the carbonylative addition reaction under syngas (CO/H_2) in CH_2Cl_2 as a solvent but in the absence of any additional amount of dppb. The yield of the unsaturated amides and the selectivity toward **4** were much lower (41% and 58% respectively) with the formation of palladium black at the end of the reaction due to the decomposition of the palladium complex (Table 1, entry 12). The use of the excess of dppb versus $Pd(OAc)_2$ seems necessary in order to stabilize the active palladium hydride intermediate species (dppp)PdH.

The control of regioselectivity of the reaction of carbonylative addition of aniline (**1a**) to 1-heptyne (**2a**) was achieved successfully. The gem-α,β-unsaturated amide (**3**) was formed as a major product using the system consisting of $Pd(OAc)_2$/dppp/*p*-TsOH/CO in THF at 120 °C, whereas the trans-α,β-unsaturated amide (**4**) was obtained as a main product by the catalytic system formed of $Pd(OAc)_2$/dppb/CO/H_2 in CH_2Cl_2 at 110 °C.

Effect of the type of phosphine ligand

The results of a previous detailed study on the effect of the type of phosphine ligand indicated clearly that the introduction of bidentate phosphine ligand was necessary for the occurrence of the reaction of the carbonylative addition of aniline (**1a**) to 1-heptyne (**1b**).[28] It was also shown that the use of monodentate phosphine ligands, such as PPh_3 or PCy_3 and others, in place of dppp or dppb gave poor results.

Among the active phosphine ligands, dppp and dppb gave the highest yields and selectivity toward the gem- or trans-α,β-unsaturated amides. Figure 1 includes a comparison between dppb and dppp under different experimental conditions (system **A**: CO/H_2, CH_2Cl_2, 110 °C, 16 h; system **B**: CO, *p*-TsOH, THF, 120 °C, 6 h). The two systems gave totally different results depending on the type of phosphine ligand. For example, the use of dppp under the experimental conditions of system **A** led to a very low total yield (10%) but the selectivity toward gem product **3** was very high (82%). However, dppp gave excellent results when it was applied with the catalytic system **B**; the total yield of the unsaturated amides achieved 94% and the selectivity toward the gem product **3** was excellent (95%). The most important and interesting results were obtained with dppb as a ligand. Dppb under the conditions of system **A** gave excellent total yield of products (**3** + **4**) but, surprisingly, the major product of the reaction was the trans-product **4**. Dppb under the conditions of system **A** led to an average yield, and the gem-α,β-unsaturated amide (**3**) was the predominant

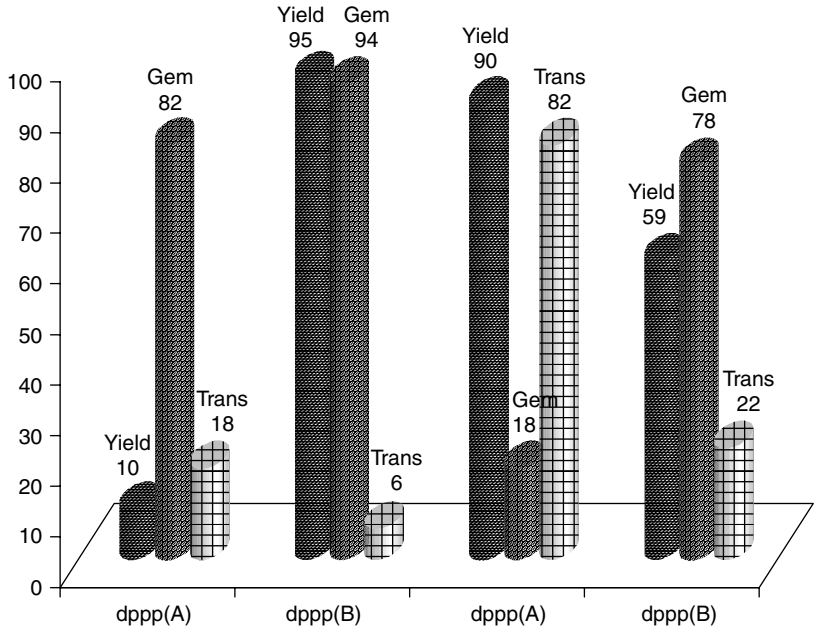


Figure 1. Palladium(II)-catalyzed carbonylative coupling of aniline (**1a**) to 1-heptyne (**2a**). Effect of the type of phosphine ligand on the total yield (**3** + **4**) and the selectivity of gem (**3**) and trans (**4**) isomers.[28] Reaction conditions: $Pd(OAc)_2$ (0.02 mmol), aniline (2.0 mmol), 1-heptyne (2.0 mmol). System **A**: dppb (0.08 mmol), CO (300 psi), H_2 (300 psi), CH_2Cl_2 (10 ml), 110 °C, 16 h. System **B**: dppp (0.04 mmol), CO (100 psi), *p*-TsOH (0.12 mmol), THF (10 ml), 120 °C, 6 h.

product (82%). There are two possible reasons to explain the formation of trans-α,β-unsaturated amide (**4**) as a major product. The first reason could be related to an electronic effect: an increase in the ligand bite angle of dppb compared with dppp increases the hydride ligand.[17] The second, more important, reason is connected to a steric effect: an increase in ligand bite angle increases the steric crowdedness around the palladium complex; as a result, hydrogen is added to the internal carbon of the terminal alkyne and subsequently leads to the formation of **4**.

Carbonylative addition of different aniline derivatives to terminal alkyl alkynes

The carbonylation of different aniline derivatives with various terminal alkynes has been successfully realized (Table 2). In addition to aniline (**1a**) and 1-heptyne (**2a**), other substrates, such as 2,4-dimethylaniline (**1b**), *p*-chloroaniline (**1c**), and *N*-methylaniline (**1d**), 1-nonyne (**2b**), 3,3-dimethyl-1-butyne (**2c**), and 5-cyanopentyne (**2d**), were adopted in the carbonylation reaction catalyzed by $Pd(OAc)_2$ under experimental conditions **A** and **B** (see legend of Fig. 1).

1-Nonyne gave very similar results to 1-heptyne in the reaction of carbonylative addition under the experimental conditions of systems **A** and **B** (Table 2, entries 1–4). 1-Heptyne has also been tested with different aniline derivatives: 2,4-dimethylaniline (**1b**), *p*-chloroaniline (**1c**) and *N*-methylaniline (**1d**; Table 2, entries 9, 10, 13, 14, 17, 18). The results were very similar in terms of yields and selectivity to the reaction with aniline (**1a**), except for *N*-methylaniline (**1d**) under the conditions of system **B** (Table 2, entry 18). The selectivity with *N*-methylaniline, which is less acidic than aniline, was lower (61%) toward the trans product **20** than the other aniline derivatives. These results reflect the important effect of the acidity of the aniline derivative on the mechanism of the formation of trans products and on the rate of the reaction. On the other hand, the carbonylation of 3,3-dimethyl-1-butyne was described to lead to the trans-α,β-unsaturated acid derivatives as the major products under various experimental conditions due to the steric hindrance of the tertiary butyl group. Surprisingly, we found that control of the regioselectivity has been totally achieved with the reaction of carbonylative addition to aniline (**1a**) catalyzed by $Pd(OAc)_2$ under system **A** or **B** (Table 2, entries 5, 6). The total yields in both reactions were very high (81–87%); the selectivity in the gem product **7** was excellent (90%) under the conditions of system **A**, and there was also excellent selectivity toward the trans product **8** obtained under the conditions of system **B**. These important results described earlier on the total control of the regioselectivity with the 3,3-dimethyl-1-butyne were also observed with other aniline derivatives, such as 2,4-dimethylaniline (**1b**), *p*-chloroaniline (**1c**), and *N*-methylaniline (**1d**; Table 2, entries 11, 12, 15, 16, 19, 20). The isolated yields ranged from 70 to 90% and there were excellent selectivities toward the gem unsaturated amides and the trans unsaturated amides, these being the major products using the conditions of systems **A** and **B** respectively.

The carbonylation of terminal alkynes by palladium(II) was affected not only by the type of the ligand and the acidity of

Table 2. Carbonylative addition of different anilines derivatives **1a–d** to terminal alkyl alkynes **2a–d**[a,b]

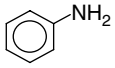
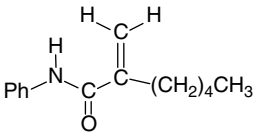
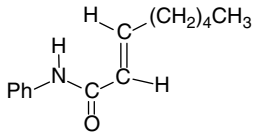
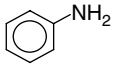
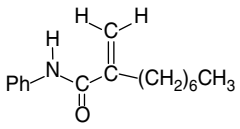
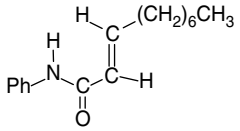
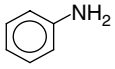
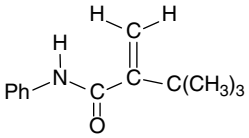
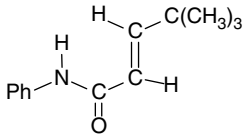
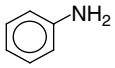
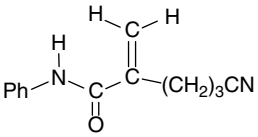
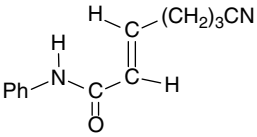
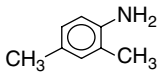
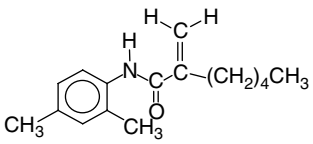
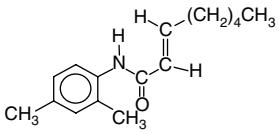
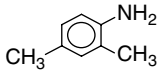
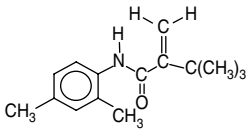
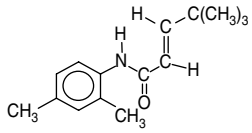
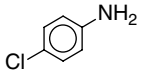
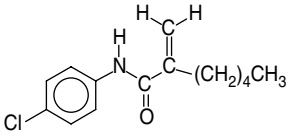
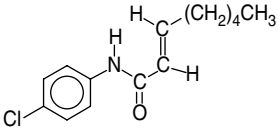
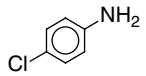
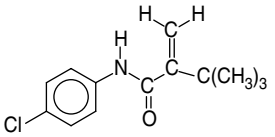
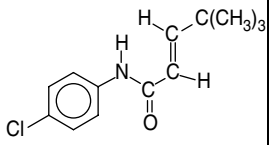
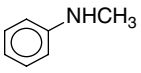
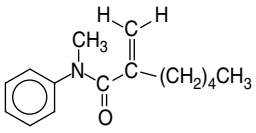
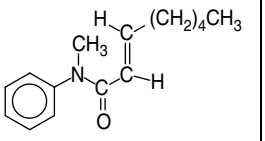
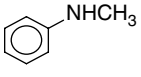
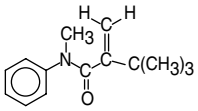
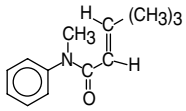
Run	Aniline derivative **1a–d**	Terminal alkyne **2a–d**	Catalytic system[b]	Yield[c] (%)	Product distribution[d]	
					Gem 3–21 (%)	*Trans* 4–22 (%)
1	 **1a**	n-C_5H_{11}–CCH **2a**	**A**	95	 **3** (95)	 **4** (5)
2			**B**	90	**3** (18)	**4** (82)
3	 **1a**	n-C_7H_{15}–CCH **2b**	**A**	90	 **5** (95)	 **6** (5)
4			**B**	82	**5** (20)	**6** (80)
5	 **1a**	$(CH_3)_3C$–CCH **2c**	**A**	81	 **7** (90)	 **8** (10)
6			**B**	87	**7** (5)	**8** (95)
7	 **1a**	CN–$(CH_2)_3$–CCH **2d**	**A**	81	 **9** (95)	 **10** (5)
8			**B**	62	**9** (32)	**10** (68)
9	 **1b**	n-C_5H_{11}–CCH **2a**	**A**	83	 **11** (95)	 **12** (5)
10			**B**	98	**11** (2)	**12** (98)
11	 **1b**	$(CH_3)_3C$–CCH **2c**	**A**	77	 **13** (92)	 **14** (8)
12			**B**	87	**13** (5)	**14** (95)
13	 **1c**	n-C_5H_{11}–CCH **2a**	**A**	91	 **15** (91)	 **16** (9)
14			**B**	92	**15** (12)	**16** (88)

Table 2. (*Continued*)

Run	Aniline derivative **1a–d**	Terminal alkyne **2a–d**	Catalytic system[b]	Yield[c] (%)	Product distribution[d]	
					gem 3–21 (%)	*trans* 4–22 (%)
15	 **1c**	$(CH_3)_3C-CCH$ **2c**	**A**	86	 **17** (86)	 **18** (14)
16			**B**	90	**17** (4)	**18** (96)
17	 **1d**	n-$C_5H_{11}-CCH$ **2a**	**A**	74	 **19** (96)	 **20** (4)
18			**B**	95	**19** (39)	**20** (61)
19	 **1d**	$(CH_3)_3C-CCH$ **2c**	**A**	70	 **21** (84)	 **22** (16)
20			**B**	75	**21** (0)	**22** (100)

[a] Reaction conditions: $Pd(OAc)_2$ (0.02 mmol), alkyne (2.0 mmol), aniline (2.0 mmol).
[b] **A**: dppp (0.04 mmol)/THF (10 ml)/*p*-TsOH (0.12 mmol)/CO (100 psi)/120 °C/6h; **B**: dppb (0.08 mmol)/CH_2Cl_2 (5 ml)/CO (300 psi)/H_2 (300 psi)/110 °C/16 h.
[c] Isolated yield.
[d] Identified and determined by GC–MS and ^1H and ^{13}C NMR.

the aniline derivative, but also by the electronic nature of the substrates. For example, the carbonylative addition of aniline (**1a**) to 5-cyano-1-pentyne (**2c**) led to high yield (81%) and excellent selectivity (95%) toward the gem product **9** under the conditions of system **A** (Table 2, entry 7). However, the trans product **10** was obtained under the conditions of system **B** with lower selectivity (68%) (Table 2, entry 8) compared with the reaction with 1-heptyne (Table 2, entry 2). It seems that the terminal carbon of the triple bond of 5-cyano-1-pentyne (**2c**) is slightly richer in electrons than the internal carbon, due to the presence of an electron-withdrawing group such as the cyano group. Therefore, protsons also attacked the terminal carbon under the conditions of system **B**, and the palladium center was probably coordinated to the internal carbon; as a result, more gem isomer was produced. The selectivity toward gem-α,β-unsaturated amides formed from the alkyl alkynes under the conditions of system **B** (Table 2) is in the order

$$CN(CH_2)_3C > CH_3(CH_2)_4C \sim CH_3(CH_2)_6C > (CH_3)_3C$$

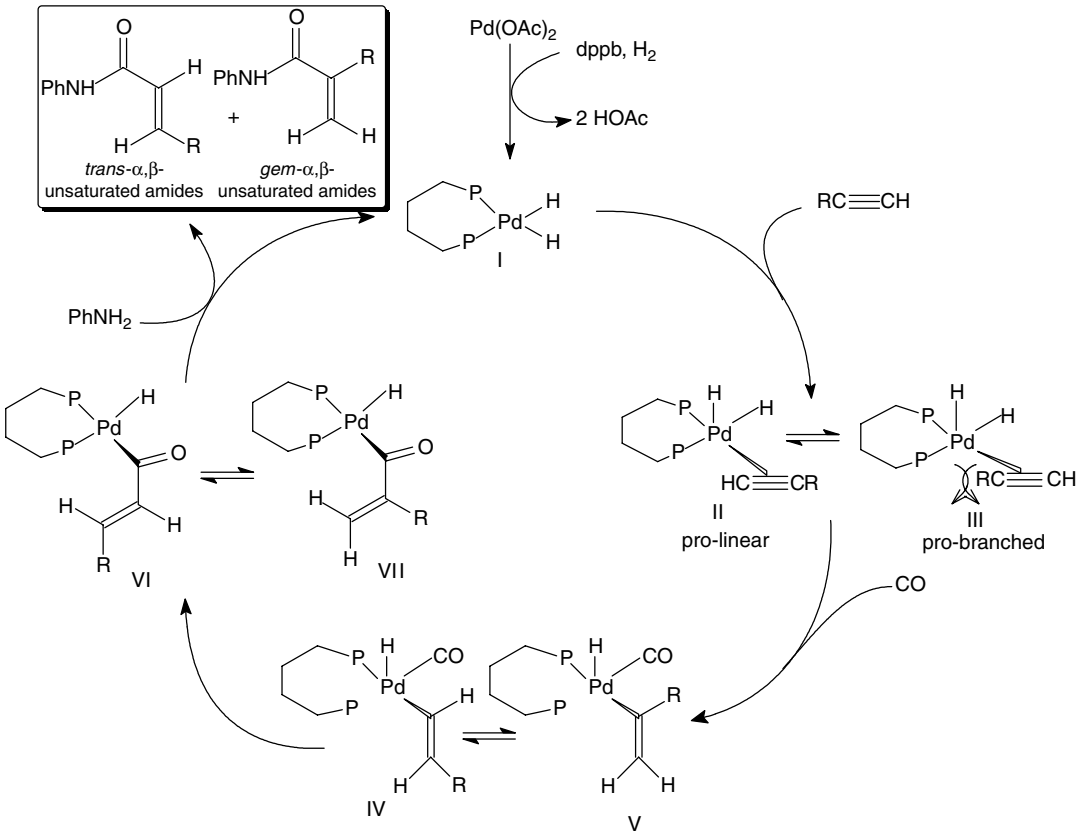
which reflects the order of electrophilicity of the terminal carbon of the triple bond.

In addition, the formation of the gem isomer as the major product with 3,3-dimethy-1-butyne under the conditions of system **A** could only be explained by the addition of a proton to the internal carbon followed by a 1,2-hydride shift to the more stable secondary carbocation where the palladium complex was attached to form the gem isomer. However, the patterns observed with 3,3-dimethyl-1-butyne under the conditions of system **B** reflect the important steric effect of the alkyl substituent. The presence of the bulky β-substituent reduced the accessibility of the active center; hence, the carbonylative addition of mono-substituted alkyl alkynes to aniline derivatives was similar to the hydrocarboxylation of mono-substituted alkyl alkynes, where the rate of the reactions decreased with the steric hindrance of the alkyl substituent.

In general, the study of the carbonylative addition of different aniline derivatives with 1-heptyne showed that the reactivity decreased in the following order:

$$p\text{-chloroaniline} > \text{aniline} > 2,4\text{-dimethylaniline} > N\text{-methylaniline}.$$

This order reflects the order of acidity of these compounds. The reactivity of aniline was enhanced by the introduction of an electron-withdrawing group on the ring, especially in the para position to the amino group, causing a decrease in electron density on the ring. This effect is transmitted to the amino group, making the nitrogen atom more deficient in electrons and, subsequently, the aniline derivative more acidic. The reverse was the case when an electron-donating



Scheme 2. Proposed mechanism for the carbonylative coupling of terminal alkynes with aniline catalyzed using a $Pd(OAc)_2$/dppb/CO/H_2 system.

group was attached to the ring. The induction time with 2,4-dimethylaniline and *N*-methylaniline was longer than with aniline, whereas the reaction for *p*-chloroaniline was completed in almost 3 h.

Proposed mechanism

The reaction of the carbonylative addition of aniline derivatives to terminal alkyl alkynes under the experimental conditions of system **A** producing the gem-α,β-unsaturated amides is very similar to hydroesterification of alkynes by different catalytic systems applied by many workers, and various mechanisms have been proposed.[13–23,29,31] However, the reaction of the carbonylative addition of aniline derivatives to terminal alkyl alkynes under the experimental conditions of system **A** producing the trans-α,β-unsaturated amides are not yet well understood in the literature. Analysis of the literature and our experimental observations led us to propose the tentative hydride mechanism shown in Scheme 2.[28]

It was demonstrated that the presence of syngas was necessary for the selective synthesis of trans-α,β-unsaturated amides. The reaction of $Pd(OAc)_2$, dppb and H_2 led probably to the palladium dihydride intermediate [(P–P)PdH_2] (**I**) with dppb bidentate to the palladium center (step I). It was mentioned previously that the addition of acetylene to [$(Cy_3P)_2$Pd(H)(HNPh)] yielded the hydrido alkynyl complex, [(Cy_3P)Pd(H)(CCH)] and aniline,[30] which indicates that the coordination of aniline was unlikely to take place in the reaction under the conditions of system **A** or **B**. It is most probable that the coordination of the alkyne (R–CCH) to the palladium center of complex **I** takes place first to give two possible intermediates, **II** and **III**. 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 **II** may be relatively more stable than the pro-branched intermediate **III**.[28] The coordination of CO to the palladium center is probably accompanied with cleavage of the Pd–P bond; dppb is now monodentate to palladium and the two intermediates **IV** and **V** are formed. The migratory insertion of CO in the alkenyl group with dppb is again bidentate to palladium and may give the key intermediates **VI** and **VII**. The reductive elimination step in the presence of H_2 would lead to the final products and regenerate the palladium hydride intermediate **I**.

CONCLUSIONS

Carbonylative addition of aniline derivatives to terminal alkyl alkynes was achieved with total control of the regioselectivity

by the reaction catalyzed by $Pd(OAc)_2$ using either the conditions of system **A** (dppp/*p*-TsOH/CO/THF) or system **B** (dppb/CO/H_2/CH_2Cl_2). Various new gem- and trans-α,β-unsaturated amides were synthesized in high yields and selectivity. The synthesis of trans-α,β-unsaturated amides was achieved in high isolated yields for the first time using a simple and efficient method. The regioselectivity of the carbonylative coupling was very sensitive to the type of ligand, solvent and the additive, and also to the use of syngas. The carbonylative coupling of primary and secondary alkylamines and diamines with terminal, internal alkyl and aromatic alkynes will also be considered in the next phase.

Acknowledgements

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