Heck Reactions Using Aryldiazonium Salts towards Phosphonic Derivatives

Heiko Brunner, Nathalie Le Cousturier de Courcy, Jean-Pierre Genêt*

Ecole Nationale Supérieure de Chimie de Paris, Laboratoire de Synthèse Sélective Organique et Produits Naturels, UMR 7523, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

Fax +33-1-44276743; E-mail: genêt@ext.jussieu.fr

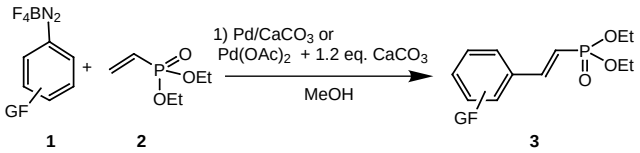
Received 15 October 1999

Abstract: A facile synthesis of aryl vinylphosphonates has been based on Heck reaction of aryldiazonium salts bearing electrowithdrawing or donating groups with vinylphosphonates. A one-pot procedure consisting of Heck reaction and hydrogenation permits the clean formation of useful Wadsworth-Emmons reagents.

Key words: Heck reaction, palladium, arenediazonium salts, hydrogenation, vinylphosphonates, Wadsworth-Emmons reactives

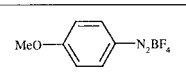
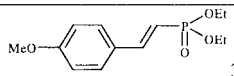
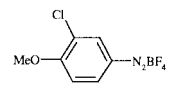
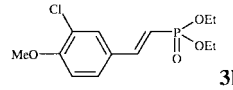
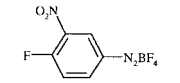
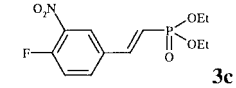
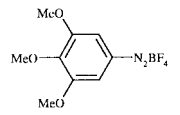
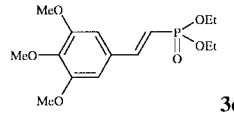
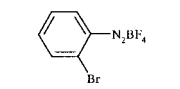
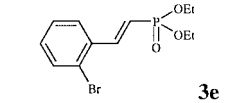
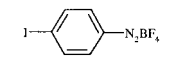
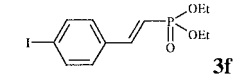
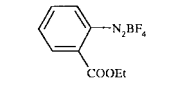
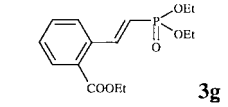
The analogues of phosphonic acids are characterized by their biological importance and have been frequently used as suitable isosteric replacements for phosphates in nucleotides, phospholipides, and sugar phosphates.[1] Furthermore, they are suitable isosters for carboxylic groups. Phosphonic acids containing amino groups in the α-,β- or γ-position have also found considerable interest for natural amino acids and are described as an important class in agricultural and medicinal chemistry.[2] It is known that these products can exert their biological activity as regulators, mediators, or enzyme inhibitors.[1,2] On the other hand phosphonates have found a wide application in organic synthesis.[3] In recent years substituted vinylphosphonates were beside their pharmacological activity[4], extensively used in polymer sciences[5] as well in organic synthesis, in particular, for preparing carbon- and heterocycles compounds.[3] Due to our recent works concerning phosphonic acid analogues we were interested in the synthesis of substituted vinylphosphonates.[6]

For their preparation non-catalytic methods, such as olefination of phosphonates bearing an active methylene group and dehydration[7,8] or dehalogenation of corresponding substituted alkylphosphonates as well as nickel catalyzed Arbusov reaction are known[9]. Currently palladium catalyzed phosphonylation with vinyl halides[10] and the phosphonylation of vinylzirconium(IV) complexes[11] are reported. Beside these methods, Heck reactions became of greater importance.[12] Next to the classical approach employing aryl halides[13] and vinyl halides[14] only palladium-catalysed phosphonylation with aryl[15] and vinyl triflates[16] as pseudohalides is described for the synthesis of aryl vinylphosphonates. Although the use of aryldiazonium salts has received a major stimulus in the Heck reaction during the last two decades[17] the use of these electrophiles for the preparation of arylated vinylphosphonates was not described to date. Wada and Oga have merely reported the reaction of an ethenephosphonate with aryldiazonium salts followed by a dehydrohalogenation of the resulting 1-chloro-2-arylalkanephosphonates.[18] However, this procedure has the disadvantage that it involves two steps and the overall yields are quite low. We were motivated to look for a more convenient synthetic pathway for arylated vinylphosphonates using aryldiazonium salts. We now report the first aerobic Heck reaction using aryldiazonium salts for preparing aryl vinylphosphonates in the presence of $Pd/CaCO_3$ and $Pd(OAc)_2/CaCO_3$ as catalytic systems[19] (Scheme 1). Compounds **3** have been prepared by using these catalytic systems (Table 1).



Scheme 1

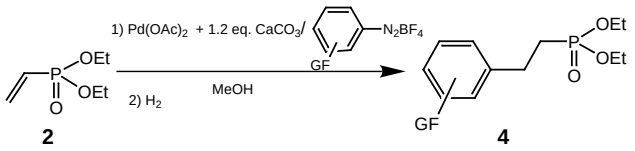
Table 1 Palladium-catalysed reaction of functionalized aryldiazonium with vinylphosphonate.

Entry	Aryldiazonium salts	Products[a]	Yield %[b]
1		 **3a**	98
2		 **3b**	96
3		 **3c**	99
4		 **3d**	93
5		 **3e**	81
6		 **3f**	92
7		 **3g**	99

[a] Reaction conditions[20]: 50 °C in methanol; 1 mmol arenediazonium salt; 0.85 mmol vinylphosphonate; 2 mol-% Pd-catalyst [b] Isolated yields.

We have found that the reaction is stereoselective and that the *E*-isomers are exclusively formed.[21] According to our previous results[19] of the Heck reaction using aryldiazonium salts we found an optimum of the reaction using methanol or ethanol at a temperature between 30 °C for electron deficient and 50 °C for electron rich arenediazonium salts within 5 min and 2 h. Thus, the use of aryldiazonium salts as electrophiles is itself characterized by more gentle reaction conditions compared with previously published palladium catalysed vinylations.

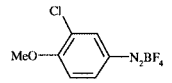
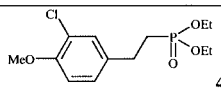
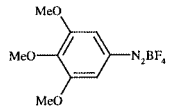
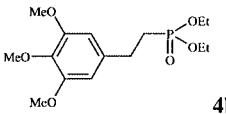
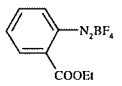
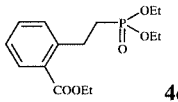
Beside these advantages this approach offers a second synthetic opportunity. The use of palladium as catalyst and of alcoholic solvents permits an one-pot procedure for the preparation of new Wadsworth-Emmons reagents combining Heck reaction and hydrogenation[22] (Scheme 2).



Scheme 2

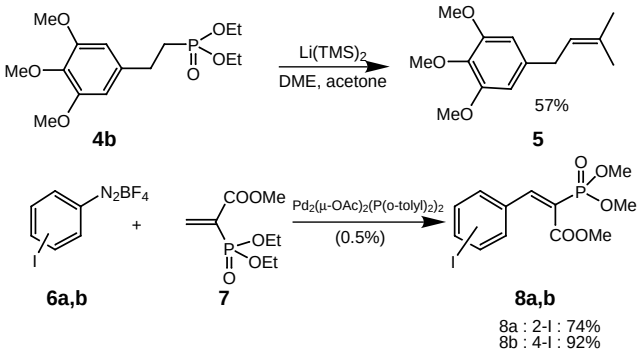
By using this protocol it is possible to gain in easily one-pot manner and in good yields several Wadsworth-Emmons reagents bearing different functional groups including chlorides and ester-groups (Table 2). In the case of halogenated arylvinylphosphonates bearing iodine or bromine atoms only the dehalogenated products could be obtained.

Table 2 Synthesis of phosphonates : one-pot Heck reaction-Hydrogenation procedure.

Entry	Aryldiazonium salts	Products[a]	Yields %[b]
1		 **4a**	99
2		 **4b**	83
3		 **4c**	98

[a] Reaction conditions: 50 °C in methanol; 1 mmol arenediazonium salt; 0.85 mmol vinylphosphonate; 2 mol-% Pd-catalyst; 1atm. H_2
[b] Isolated yields.

In regard of prenylated phenolic moieties (like **4b**), which represent a widespread motif in the structure of natural products isolated from plants and fungi[23] this strategy allows an elegant application in organic synthesis in particular for natural products[24] (Scheme 3).



Scheme 3

However not only unsubstituted vinylphosphonates, but also α–substituted vinylphosphonates like trimethyl 2-phosphonoacrylate **7** were reacted with arenediazonium salts.[25] Instead of $Pd(OAc)_2/CaCO_3$ or $Pd/CaCO_3$ as catalytic system, the use of the palladacycle[26,27] $Pd_2(\mu\text{-}OAc)_2(P(o\text{-tolyl})_2)_2$ was also feasible in methanol under aerobic conditions and gave good yields (Scheme 3).

The coupling constants $^3J_{PH} = 24.5$ Hz in the ^1H NMR-spectra indicate that the stereochemistry corresponds to an *E*-configuration on the basis of the phosphorous-*cis* vinyl proton NMR.[28,29] Furthermore it is very remarkable that not only iodine-substitution in *para*-position but also in *ortho*-position is completely compatible with this reaction. In the light of practicability we emphasise that this approach using $Pd_2(\mu\text{-}OAc)_2(P(o\text{-tolyl})_2)_2$ as catalytic system can also be carried out under aerobic conditions using not degassed solvents.[28]

In conclusion, this protocol is characterized by the mild conditions and an excellent variety of functional groups tolerated and promises to be an useful method for the introduction of vinyl- and ethylene phosphonate functionalities into organic substrates. This method permits also the synthesis of arylated vinyl phosphonates bearing iodide and bromide functionalities via Heck reactions. Further investigations concerning phosphonic analogues are currently underway in our laboratory.

Acknowledgement

H.B. thanks the exchange program between CNRS and Max-Planck-Gesellschaft for a post-doctoral scholarship. N. de Courcy. thanks the CROUS for a scholarship (Allocation Spéciale 3ème cycle). Financial support by the CNRS is gratefully acknowledged.

References and Notes

(1) Engel, R. *Chem. Rev.* **1977**, *77*, 349-367. Klachburn, G.M.; Perree, T.D. *Chem. Scr.* **1986**, *26*, 21.

(2) Kafarski, P.; Lejczak, B. *Phosphorus, Sulfur Silicon Relat. Elem.* **1991**, *63*, 193-215. O'Donnell, M.J.; Lawley, L.K.; Pushpavanam, P.B.; Burger, A.; Bordwell, F.G.; Zhang, X.-M. *Tetrahedron Lett.* **1994**, *35*, 6421-6424 and literature cited therein; for a recent review on racemic and optically active synthesis of α-aminophosphonic acids see Uziel, J.; Genêt, J.-P. *Russ. J. Org. Chem.* **1997**, *33*, 1521-1542.
(3) Minami, T.; Motoyoshiya, J. *Synthesis* **1992**, 333-349.
(4) several examples of pharmaceutical active arylated vinyl-phosphonates are published in the literature of patents e.g. Graeve, R.; Thorwart, W.; Raiss, R.; Weithmann, K.U.; Mullner, S., US 5,627,173 (Hoechst AG **1997**). Lennon, P.J., US 5,434,288 (Monsanto Company **1995**).
(5) *Römpp Lexikon Chemie* 10; Falbe, J.; Regitz, M., Eds.; Georg Thieme Verlag: Stuttgart; Vol. 6 1999. Jin, S.; Gonsalves, K.E., *Macromolecules* **1998**, *31*, 1010-1015 and literature cited therein. Davies, K.P.; Walker, D.R.E.; Woodward, G.; Smith, A.C., EP 861846 A2 (Albright & Wilson Ltd **1998**). For applications in the field of flame retardancy in styrenic and acrylic polymers with covalently bound phosphorous-containing groups see Ebdon, J.R, *Recent Adv. Flame Retard. Polym. Materials* **1997**, *8*, 161.
(6) Henry, J.C.; Lavergne, D.; Ratovelomanana-Vidal, V.; Beletskaya, I. P.; Dolgina, T.M. *Tetrahedron Lett.* **1998**, *39*, 3473-3476.
(7) Ahlbrecht, H.; Farnung, W. *Synthesis* **1977**, 336-338. Venugopalan, B.; Bevin Hamlet, A.; Durst, T. *Tetrahedron Lett.* **1981**, *22*, 191-194.
(8) Minami, T.; Nishimura, K.; Hirao, I.; Suganuma, H.; Agawa, T. *J. Org. Chem.* **1982**, *47*, 2360-2363 and literature cited therein.
(9) Tavs, P.; Weitkamp, H. *Tetrahedron* **1970**, *26*, 5529-5534.
(10) Hirao, T.; Masunaga, Y.; Ohshiro, T.; Agawa, T. *Tetrahedron Lett.* **1980**, *21*, 3595-3598. Hirao, T.; Masunaga, T.; Agawa, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 909-913.
(11) Zhong, P.; Huang, X.; Xiong, Z.-X. *Synlett* **1999**, 721-722.
(12) Milton, L.; Donald, M. *Phosphorus* **1974**, *4*, 63.
(13) Xu, Y.; Jin, X.; Huang, G.; Huang, Y. *Synthesis* **1983**, 556-558. Demik, N.N.; Kabachnik, M.M.; Novikova, Z.S.; Beletskaya, I.P. *Russ. J. Org. Chem.* **1995**, *31*, 57-60. and *Zh. Org. Khim.* **1995**, *31*, 64-68. Ortwine, D.F.; Malone, T.C.; Bigge, C.F.; Drummond, J.T.; Humblet, C.; Johnson, G.; Pinter, G.W. *J.Med.Chem.* **1992**, *35*, 1345-1370. Bigge, C.F; Johnson, G.; Ortwine, D.F.; Drummond, J.T.; Retz, D.M.; Brahce, L.J.; Coughenour, L.L.; Marcoux, F.W.; Probert, A.W., Jr. *J. Med. Chem.* **1992**, *35*, 1371-1384.
(14) Axelrad, G.; Laosooksathit, S.; Engel, R. *J. Org. Chem.* **1981**, *46*, 5200-5204.
(15) Petrakis, K.S.; Nagabhushan, T.L. *J.Am.Chem.Soc.* **1987**, *109*, 2831-2833.
(16) Burini, A.; Cacchi, S.; Pace, P.; Pietroni, B.R. *Synlett* **1995**, 677-679. Holt, D.A.; Erb, J.M. *Tetrahedron Lett.* **1989**, *30*, 5393-5396.
(17) For some recent works in this area : see Beller, M., Kühlein,K., *Synlett* **1995**, 441-442. Ikenaga, K.; Matsumoto, S.; Kikukawa, K.; Matsuda, T., *Chem.Lett.* **1988**, 873-876. Sengupta, S., Sadhukhan, S.K., *Tetrahedron Lett.* **1998**; *39*, 715-718. Sengupta, S., Sadhukan, S.K., Bhattacharyya, S., Guha, J., *J. Chem. Soc., Perkin Trans 1* **1998**, 407-410.
(18) Wada, Y.; Oda, R. *Kogyo Kagaku Zasshi* **1964**, *67*, 2093. C.A. **1965**, *62*, 13177.
(19) Brunner, H., Le Cousturier de Courcy, N.; Genêt, J-P. *Tetrahedron Lett.* **1999**, *40*, 4815-4818.
(20) *Preparation of aryldiazonium salts* : Roe, A. *Org. React.* **1949**, *5*, 193-228. Doyle, M.P.; Bryker, W.J. *J. Org. Chem.* **1979**, *44*, 1572-1574. *Typical procedure:* In a reaction flask 1 mmol of the corresponding aryldiazonium salt, 0.02 mmol of the Pd-catalyst and 1 mmol of $CaCO_3$ were suspended in 5 mL of solvent at room temperature. Subsequently 0.85 mmol of the vinylphosphonate was added at room temperature and the resulting mixture was stirred at 50 °C. The progress of the reaction was monitored by measuring the volume of given off gas (5 min – 2 h). After the reaction was completed the solvent was evaporated and the residue was purified by flash chromatography on silica.
(21) The stereochemistry was determinated by ^{1}H NMR spectroscopy. In all cases the coupling constants $^3J_{HH}$ indicate an *E*-configuration. Characteristic NMR-data:
3a: ^{1}H NMR δ ($CDCl_3$) 7.46-7.27 (m, 3H), 6.80 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 2.4 Hz, 2H), 6.00 (t, $^3J_{HH}$ = 17.6 Hz, 1H), 4.03 (quint. $^3J_{HH}$ = 7.1 Hz, 4H), 3.74 (s, 3H), 1.26 (t, $^3J_{HH}$ = 7.1 Hz, 6H); ^{13}C NMR δ ($CDCl_3$) 161.1 (s), 148.2 (d, $^2J_{CP}$ = 6.1 Hz, CH), 129.1 (d), 124.0 (s), 114.0 (d), 110.7 (d, $^1J_{CP}$ = 191.6 Hz, CH), 61.6 (t, $^2J_{CP}$ = 5.9 Hz), 55.1 (q), 16.20 (q).
3b: ^{1}H NMR: δ ($CDCl_3$) 7.64-7.25 (m, 3H), 7.07 (d, $^3J_{HH}$ = 8.5 Hz, 1H), 6.31 (t, $^3J_{HH}$ = 17.8 Hz, 1H), 4.11 (quint. $^3J_{HH}$ = 7.5 Hz, 4H), 3.90 (s, 3H), 1.31 (t, $^3J_{HH}$ = 7.0 Hz, 6H); ^{13}C NMR δ ($CDCl_3$) 158.1 (s), 148.7 (d, $^2J_{CP}$ = 6.7 Hz, CH), 136.9 (s), 129.4 (d), 124.0 (s), 113.4 (d), 112.8 (d, $^1J_{CP}$ = 191.3 Hz, CH), 63.4 (t, $^2J_{CP}$ = 5.5 Hz), 56.9 (q), 16.8 (q).
3c: ^{1}H NMR: δ (CD_3OD) 8.85-8.74 (m, 1H), 8.53-7.76 (m, 3H), 7.10 (td, $^3J_{HH}$ = 17.5 Hz, $^4J_{HH}$ = 2.9 Hz, 1H), 4.75 (quint., $^3J_{HH}$ = 6.2 Hz, 4H), 2.01 (t, $^3J_{HH}$ = 6.2 Hz, 6H); ^{13}C NMR δ (CD_3OD) 154.5 (s, $^1J_{CF}$ = 258.9 Hz), 148.3 (d, $^2J_{CP}$ = 8.4 Hz), 136.1 (d, $^3J_{CF}$ = 8.6 Hz), 134.0 (s, $^3J_{CF}$ = 8.4 Hz), 127.8 (d, $^2J_{CF}$ = 22.6 Hz), 121.5 (s, $^2J_{CF}$ = 22.0 Hz), 116.9 (d, $^1J_{CP}$ = 189.6 Hz), 64.1 (t, $^2J_{CP}$ = 5.5 Hz), 17.9 (q).
3d: ^{1}H NMR δ ($CDCl_3$) 8.25 (t, $^3J_{HH}$ = 17.6 Hz, 1H), 6.57 (s, 2H), 6.25 (t, $^3J_{HH}$ = 17.6 Hz, 1H), 4.14 (quint., $^3J_{HH}$ = 7.5 Hz, 4H), 3.82 (s, 6H), 3.74 (s, 3H), 1.35 (t, $^3J_{HH}$ = 7.1 Hz, 6H); ^{13}C NMR δ ($CDCl_3$) 149.2 (d, $^2J_{CP}$ = 6.9 Hz), 144.3 (s), 132.8 (s), 118.4 (d, $^1J_{CP}$ = 194.4 Hz), 107.3 (d), 62.4 (t, $^2J_{CP}$ = 5.0 Hz), 56.4 (q), 52.3 (q), 13.8 (q).
3e: ^{1}H NMR δ ($CDCl_3$) 7.62 (t, $^3J_{HH}$ = 17.5 Hz, 1H), 7.50 (dd, $^3J_{HH}$ = 6.0 Hz, $^4J_{HH}$ = 1.7 Hz, 2H), 7.27-7.07 (m, 2H), 6.16 (t, $^3J_{HH}$ = 17.5 Hz, 1H), 4.07 (quint., $^3J_{HH}$ = 7.0 Hz, 4H), 1.28 (t, $^3J_{HH}$ = 7.0 Hz, 6H); ^{13}C NMR δ ($CDCl_3$) 146.3 (d, $^2J_{CP}$ = 7.6 Hz), 133.2 (d), 131.0 (d), 127.6 (d), 127.4 (d), 124.6 (s), 117.5 (d, $^1J_{CP}$ = 189.3 Hz), 61.9 (t, $^2J_{CP}$ = 5.5 Hz), 16.3 (q).
3f: ^{1}H NMR δ ($CDCl_3$) 8.22 (t, $^3J_{HH}$ = 18.0 Hz, 1H), 7.73 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.23 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 6.23 (t, $^3J_{HH}$ = 18.0 Hz, 1H), 4.25 (quint., $^3J_{HH}$ = 7.0 Hz, 4H), 1.39 (t, $^3J_{HH}$ = 7.1 Hz, 1H); ^{13}C NMR δ ($CDCl_3$) 148.0 (d, $^2J_{CP}$ = 7.0 Hz), 138.0 (d), 133.5 (s), 129.6 (d), 117.2 (d, $^1J_{CP}$ = 192.4 Hz), 97.4 (s), 62.1 (t, $^2J_{CP}$ = 5.0 Hz), 14.2 (q).
3g: ^{1}H NMR δ ($CDCl_3$) 8.21 (t, $^3J_{HH}$ = 19.9 Hz, 1H), 7.97 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.4 Hz, 1H), 7.61-7.40 (m, 3H), 6.16 (t, $^3J_{HH}$ = 19.8 Hz, 1H), 4.40 (q, $^3J_{HH}$ = 7.1 Hz, 2H), 4.19 (quint. $^3J_{HH}$ = 7.0 Hz, 4H), 1.39 (t, $^3J_{HH}$ = 7.1 Hz, 9H); ^{13}C NMR δ ($CDCl_3$) 166.3 (s), 147.8 (d, $^2J_{CP}$ = 7.0 Hz), 136.5 (s), 132.1 (d), 130.3 (d), 129.2 (d), 127.4 (d), 119.8 (s), 116.1 (d, $^1J_{CP}$ = 189.6 Hz), 62.1 (t, $^2J_{CP}$ = 4.5 Hz), 60.39 (t), 16.1 (q), 13.9 (q).
(22) To our knowledge some examples using one-pot sequences Heck reaction – hydrogenation are known: Meyer, W.; Reinehr, D.; Oertle, K.; Schurter, R., EP 0 102 925 A2 and EP 0 248 245 A2 (Ciba-Geigy **1983**). Bräse, S.; Schroen, M. *Angew. Chem. Int. Ed.* **1999**, *38*, 1071-1073. *Typical procedure:* In a reaction flask 1 mmol of the corresponding aryldiazonium salt, 0.02 mmol of the Pd-catalyst and 1 mmol of $CaCO_3$ were suspended in 5 mL of solvent at room temperature. Subsequently 0.85 mmol of the vinylphosphonate was added at room temperature and the resulting mixture was stirred at 50 °C. The progress of the

reaction was monitored by measuring the volume of given off gas (15 min – 2 h). After the Heck reaction was completed the mixture was cooled to room temperature and stirred at room temperature under hydrogen (1 atm). The progress of the reaction was monitored TLC (1 – 2 days). After the hydrogenation was completed the solvent was evaporated and the residue was purified by flash chromatography on silica.

(23) Donnelly, D.M.X.; Boland, G.M. *Nat. Prod. Rep.* **1995**, *12*, 321-338.

(24) Huneck, S.; Connolly, J.D.; Harrison, L.J.; Joseph, R.S.I.; Pocs, T. *Phytochemistry* **1984**, *23*, 2396-2397.

(25) For the reaction conditions see Yue, X.; Li, Y. *Synthesis* **1996**, 736-740. The spectroscopical data were identical to previously reported data.[24]

(26) Herrmann, W.A.; Broßmer, C.; Öfele, K.; Reisinger, C.-P.; Priermeier, T.; Beller, M.; Fischer, H. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1844-1848. Beller, M.; Fischer, H.; Herrmann, W.A.; Öfele, K.; Broßmer, C. *Angew. Chem. Int. Ed. Engl.* **1995**, *37*, 1848-1849. Herrmann, W.A; Broßmer, C.; Reisinger, C.-P.; Riermeier, T.H.; Öfele, K.; Beller, M. *Chem. Eur. J.* **1997**, *3*, 1357-1364. Herrmann, W.A.; Reissinger, C.-P.; Öfele, K.; Broßmer, C.; Beller, M.; Fischer, H. *J. Mol. Catal.* **1996**, *103*, 133-146. Beller, M.; Riermeier, H. *Tetrahedron Lett.* **1996**, *37*, 6535-6538. Beller, M.; Riermeier, H.; Haber, S.; Kleiner, H.J.; Herrmann, W.A. *Chem. Ber.* **1996**, *129*, 1259-1264.

(27) A new review article concerning the catalytic applications of the palladacycle *trans*-di(μ-acetato)-bis[o-(di-*o*-tolylphosphino)benzyl]dipalladium(II) in cross couplings was recently published by Speicher, A; Schulz, T.; Eicher, T. *J. Prakt. Chem.* **1999**, *341*, 605.

(28) *Typical procedure for the synthesis of* **8b***:* In a reaction flask 318 mg (1mmol) 4-iodobenzenediazoniumtetrafluoroborate, 9.4 mg (0.01mmol ≅ 0.5mol-% Pd) *trans*-di(μ-acetato)-bis[o-(di-*o*-tolylphosphino)benzyl]dipalladium(II) were suspended in 5mL methanol. Subsequently 0.14 mL (0.9mmol) methyl-2-(diethylphosphono)acrylate was added and the reaction mixture was stirred at 50 °C. After the reaction was completed the solvent was evaporated and the residue was chromatographed on silica gel eluting with cyclohexane/EtOAc mixture (30/70 v/v) to give 327 mg (92%) of **8b** as white solid: mp:142 °C; ^{1}H NMR δ (CD_3OD) 8.30 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 2.2 Hz, 2H), 7.73 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 2.2 Hz, 2H), 7.37 (t, $^3J_{PH}$ = 24.5Hz), 3.80 (s, 3H) 3.72 (d, $^3J_{PH}$ = 10.1 Hz, 6H); ^{13}C NMR δ (CD_3OD) 166.5 (d, J_{CP} = 13.2 Hz), 149.2 (d, J_{CP} = 6.2 Hz), 142.2 (s), 139.4 (d), 137.2 (d), 115.3 (d, J_{CP} = 190.2 Hz), 97.6 (s), 53.7 (q, J_{CP} = 5.6 Hz), 52.9 (q); IR (KBr) 1718, 1254; MS m/s (relative intensity) 384 (M^+, 6).

(29) Aboujaoude, E.E.; Lietjé, S.; Collignon, N.; Teulade, M.P.; Savignac, P. *Tetrahedron Lett.* **1985**, *26*, 4435-4438. Minami, T.; Utsonomiya, T.; Nakamura, S.; Okubo, M.; Kitamura, N; Okada, Y.; Ichikawa, J. *J. Org. Chem.* **1994**, *59*, 6717-6727.

Article Identifier:
1437-2096,E;2000,0,02,0201,0204,ftx,en;G24999ST.pdf