

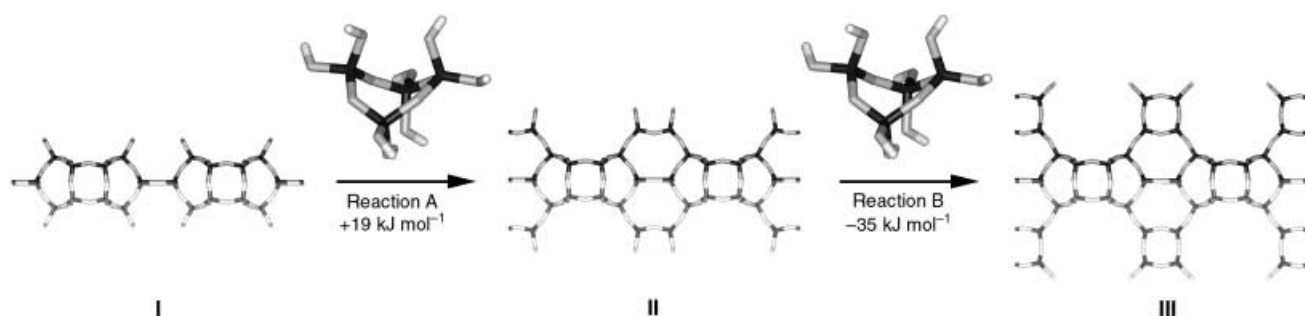


Figure 5. The S4R-mediated reaction pathway. The reaction proceeds by the addition of an S4R to the type I surface, giving the type II surface and further S4R condensation to give the type III surface. Color code as in Figure 1.

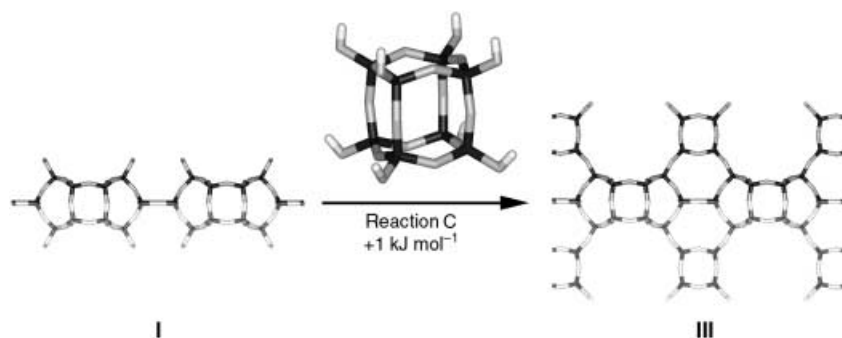


Figure 6. The D4R-mediated reaction pathway. The reaction proceeds by a one-step condensation of a D4R species onto the type I surface to give the type III surface. Color code as in Figure 1.

cally unfavorable but even at relatively moderate temperatures, this reaction would be expected to proceed.

Given these findings, the evidence suggests that termination II, the surface structure expected to be stable on the grounds of surface energy, but not observed by HREM,^[3] is either not formed, or quickly reacts to give the D4R-terminated surface. By contrast, condensation of a D4R unit on the type I surface is predicted to occur under reaction conditions. The addition of this unit gives a route from the type I to type III surface, which does not require formation of the type II surface and therefore may also explain why the type II surface is not observed. Given recent synthetic findings, the process of condensation which gives rise to the D4R unit is clearly accelerated by the presence of fluoride ions. We speculate that the fluoride ion lowers the activation barrier that separates reagents from the D4R unit and other products but will address this point directly in future work.

In summary, we have demonstrated that relatively simple interatomic potential calculations are able to reproduce the surface structures observed by using HREM imaging. Additionally, direct assessment of the crystal growth process reveals that one possible termination is not formed or is likely to be a short-lived intermediate that accounts directly for its absence in HREM imaging experiments. More fundamentally, the results provide evidence that the nanoscopic surface structures arise not simply from optimal packing of silicate tetrahedra but from the complex reactions of siliceous oligomers with the zeolite surface.

Received: October 17, 2001
Revised: February 14, 2002 [Z18075]

- [1] J. M. Newsam, M. M. J. Treacy, W. T. Koestler, C. B. de Gruyter, *Proc. R. Soc. London Ser. A* **1998**, 420, 375.
- [2] J. B. Higgins, R. B. LaPierre, J. L. Schlenker, A. C. Rohrer, J. D. Wood, G. T. Kerr, *Zeolites* **1988**, 8, 446.
- [3] Z. Liu, T. Ohsuna, O. Terasaki, M. A. Camblor, M.-J. Diaz-Cabanas, K. Hiraga, *J. Am. Chem. Soc.* **2001**, 123, 5370.
- [4] M. J. Sanders, M. Leslie, C. R. A. Catlow, *J. Chem. Soc. Chem. Commun.* **1984**, 1271.
- [5] L. Whitmore, B. Slater, C. R. A. Catlow, *Phys. Chem. Chem. Phys.* **2000**, 2, 5354.
- [6] J. D. Gale, *J. Chem. Soc. Faraday Trans.* **1997**, 93, 629–637.
- [7] J. D. H. Donnay, D. Harker, *Am. Mineral.* **1937**, 22, 446.
- [8] D. H. Gay, A. L. Rohl, *J. Chem. Soc. Faraday Trans.* **1995**, 91, 925.
- [9] Version 4.2, Cerius² 4.2 Users Guide, Molecular Simulations Inc., **1999**.
- [10] C. R. A. Catlow, D. S. Coombes, D. W. Lewis, J. C. G. Pereira, *Chem. Mater.* **1998**, 10, 3249–3265.

Pd-Catalyzed Decarbonylative Olefination of Aryl Esters: Towards a Waste-Free Heck Reaction**

Lukas J. Gooßen* and J. Paetzold

*Dedicated to Dr. Manfred Jautelat
on the occasion of his retirement*

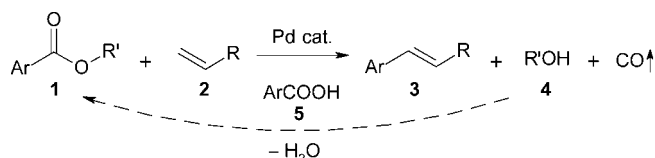
Over the last years, the Heck reaction has found widespread use in preparative laboratories and in industrial applications as a mild and efficient method for the regioselective attachment of side chains to aromatic rings.^[1] Besides the standard aryl halides, various aryl sources such as aryl triflates,^[2]

[*] Dr. L. J. Gooßen, J. Paetzold
Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr (Germany)
Fax: (+49) 208-306-2985
E-mail: goossen@mpi-muelheim.mpg.de

[**] We thank L. Winkel for technical assistance, Prof. Dr. M. T. Reetz for generous support and constant encouragement, and the DFG, the FCI, and the BMBF for financial support.

diazonium salts,^[3] sulfonyl halides,^[4] and aroyl halides^[5] have been utilized, and highly efficient catalyst systems have been developed.^[6] However, for all these compounds, stoichiometric amounts of base are required, and the equivalent amounts of waste salts are produced. De Vries and co-workers first presented a possible solution to this long-standing problem when they utilized aromatic carboxylic acid anhydrides as aryl sources.^[7] In the presence of a PdCl₂/NaBr catalyst system, carboxylic anhydrides were cleanly converted into one equivalent of the corresponding vinyl arenes and one equivalent of the carboxylic acids, which, in principle, can be converted back into the starting anhydride. However, for most carboxylic acids, the dehydration reaction does not occur readily and is usually not waste-free either.^[8]

Herein we report the first example of a Heck reaction in which the by-product can be recycled efficiently so that only CO and water are produced as waste. Our strategy to make efficient use of the widely available carboxylic acids as substrates for the Heck reaction while overcoming the limitations of the previous protocols was to perform the olefination with carboxylic acid derivatives that are less reactive and more easily accessible than anhydrides, that is, with esters.^[9] We found a palladium catalyst that is able to insert into the carbon–oxygen bond of an ester, thus entering a catalytic cycle similar to the one postulated for the Heck reaction of carboxylic acid anhydrides.^[7, 10] After the oxidative addition of the ester to the palladium center, extrusion of carbon monoxide leads to the formation of an aryl–palladium complex, and after insertion of the olefin, β -hydride elimination liberates the desired vinyl arene and the alcohol by-product. The alcohol can then be recycled back into the starting ester by reaction with fresh carboxylic acid by using standard esterification techniques (Scheme 1). In this case,



Scheme 1. Decarbonylative Heck olefination of esters.

CO and water are the only by-products in the overall reaction.

The key step towards realizing this highly desirable process was to identify a catalyst system capable of activating carboxylic esters. We thus screened various catalysts under different conditions for the model reaction of *p*-nitrophenyl benzoate (**1a**) and styrene **2a** (Scheme 1, Ar = Ph, R = Ph, R' = *p*-NO₂C₆H₄). *p*-Nitrophenyl esters are particularly attractive substrates because they can be generated within minutes in quantitative yields from various functionalized carboxylic acids and commercially available nitrophenyl chloroformate.^[11] Selected results of our screening experiments are shown in Table 1.

Palladium chloride was identified to be the best precatalyst (Table 1, entries 1–3), and the addition of alkali metal halides proved to increase the effectiveness of the catalyst further (Table 1, entries 4–11).^[7, 12] Among these, the cheap and easily separable lithium chloride was found to be as effective

Table 1. Reaction of nitrophenyl benzoate with styrene.

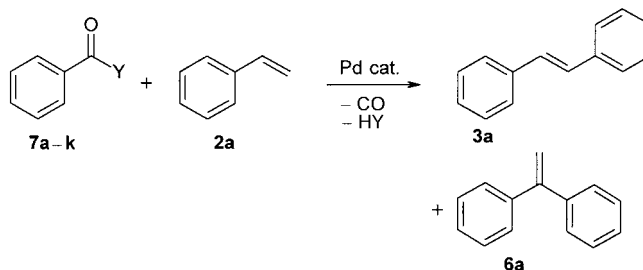
Entry	Pd source	Additive	Ligand	Conversion [%]	Selectivity [%]
1	Pd(OAc) ₂	–	–	< 2	> 90
2	(dba) ₃ Pd ₂	–	–	< 2	> 90
3	PdCl ₂	–	–	12	90
4	PdCl ₂	LiCl	–	60	> 95
5	PdCl ₂	LiBr	–	39	> 95
6	PdCl ₂	KCl	–	24	> 95
7	PdCl ₂	KBr	–	30	> 95
8	PdCl ₂	NaCl	–	31	> 95
9	PdCl ₂	NaBr	–	35	> 95
10	PdCl ₂	TBACl	–	36	90
11	PdCl ₂	TBABr	–	56	90
12	PdCl ₂	LiCl	PPh ₃	22	75
13	PdCl ₂	LiCl	Picoline	69	> 95
14	PdCl ₂	LiCl	Quinoline	67	80
15	PdCl ₂	LiCl	Isoquinoline	91	> 95
16 ^[a]	PdCl ₂	LiCl	Isoquinoline	44	> 95

Conditions: nitrophenyl benzoate (1 mmol), styrene (1.2 mmol), Pd source (0.03 mmol), additive (0.09 mmol), ligand (0.1 mmol), NMP, 16 h, 160 °C. Conversions and selectivities were determined by GC analysis, with tetradecane as internal standard. [a] The reaction was performed with 0.3 mol % catalyst. NMP = *N*-methylpyrrolidone.

as tetra-*n*-butylammonium bromide (Table 1, entries 4, 11). Without the addition of stabilizing ligands, the reaction initially proceeded with a fast turnover. However, complete precipitation of the catalyst and loss of catalytic activity was observed before full conversion of the substrate. The addition of amines significantly slowed down the reaction, but greatly enhanced the stability of the catalyst so that higher yields were obtained (Table 1, entries 13–15). The starting material was almost fully converted within a reasonable reaction time when isoquinoline or substituted pyridines were used as ligands. Phosphanes coordinate more strongly and therefore inhibit the reaction (Table 1, entry 12).

The ideal amount of catalyst is 3 mol %, but even with a significantly lower catalyst loading, moderate yields are obtained (Table 1, entry 16). Similarly to the standard Heck olefinations, the olefin did not insert into the aryl–palladium bond with complete regioselectivity, so that in all cases a 13:1 mixture of the products **3a** and **6a** was obtained (Scheme 2).^[13]

We next investigated the range of acid derivatives that can be converted with the optimized catalyst system (Scheme 2; Table 2). Benzoates of various electron-deficient phenols were found to be suitable substrates (Table 2, entries 1–4). Expectedly, the ester of highly acidic pentafluorophenol is most reactive, but reaction turnover was observed even with poorly activated *p*-CF₃-phenol (Table 2, entries 5). Unfortu-



Scheme 2. Decarbonylative Heck olefination of benzoic acid derivatives.

Table 2. Variation of the benzoic acid derivative.

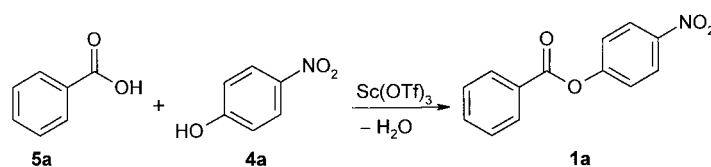
Entry	Y	Yield (3+6) [%] ^[a]	Entry	Y	Yield (3+6) [%] ^[a]
1		94	7	O-CH ₃	–
2		53	8		51
3		30	9		68
4		77	10		25
5		13	11		10
6		trace	12		10 ^[b]

Conditions: benzoic acid derivative (1 mmol), styrene (1.2 mmol), PdCl₂ (0.03 mmol), LiCl (0.09 mmol), isoquinoline (0.3 mmol), NMP, 16 h, 160 °C. [a] The yields were determined by GC analysis, with tetradecane as internal standard. In all cases, except entry 12, 13:1 mixtures of the isomers **3** and **6** were formed in >95 % selectivity; [b] Full conversion, isobutene was the main product.

nately, only trace amounts of product were observed in the reactions with esters of alkanols or phenol itself (Table 2, entries 6, 7).

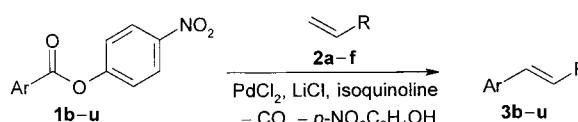
Besides phenol esters, acid derivatives with similar activity, for example, hydroxysuccinimides and imidazolidones, were also converted by the catalyst system in reasonable yields (Table 2, entries 8–10). Vinyl esters would have been particularly interesting substrates since the volatile acetaldehyde is the only by-product in the olefination reaction. However, only modest conversions were observed for this type of substrate (Table 2, entry 11). Surprisingly, the mixed anhydride of benzoic acid and pivalic acid, which was successfully employed in other Pd-catalyzed reactions,^[14] did not react with the desired regioselectivity: instead of stilbene and pivalic acid, isobutene and benzoic acid were the main products (Table 2, entry 12).

To demonstrate the viability of our concept for a waste-free Heck olefination, we looked for a catalytic method to generate activated *p*-nitrophenyl esters directly from carboxylic acids and the alcohol, hence avoiding the use of stoichiometric amounts of a dehydrating agent. We screened several esterification catalysts under various conditions for the model reaction of nitrophenol with benzoic acid (Scheme 3). Although only moderate yields were observed with standard dehydration catalysts,^[15] for example, sulfuric acid (61 %), *p*-toluenesulfonic acid (45 %), or HfCl₄ (5 %), the desired conversion gave good yields in the presence of Sc(OTf)₃ (3 mol %) at 160 °C in the absence of solvent (83 %) or in *o*-dichlorobenzene (56 %). Thus, nitrophenol is recycled and a waste-free process is possible.



Scheme 3. Conversion of benzoic acid into the nitrophenol ester.

The scope of the new Heck olefination was investigated by using various combinations of *p*-nitrophenyl carboxylates and olefins (Scheme 4, Table 3). Electron-deficient carboxylic

Scheme 4. Heck olefination of *p*-nitrophenyl carboxylates.

esters were found to react faster and to give better yields than electron-rich derivatives, but even the electron-rich *p*-MeO-stilbene is still accessible in a satisfactory yield (Table 3, entry 1). Many functional groups are tolerated: carboxylic esters that contain halo, keto, cyano, formyl, nitro, or protected amino groups were successfully converted (**3a–m**). The important class of heterocyclic carboxylic esters was also suitable as starting materials (**3n**, **3o**). The decarbonylative Heck olefination of the widely available α,β -unsaturated carboxylic esters (**3p**) could also be particularly useful, since the availability of the synthetically equivalent vinyl halides is rather limited.

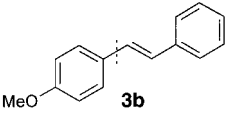
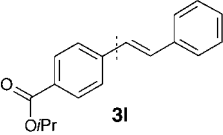
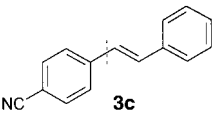
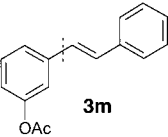
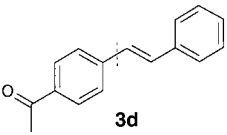
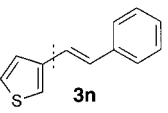
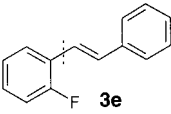
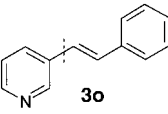
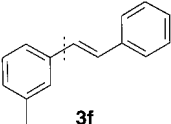
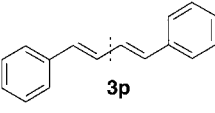
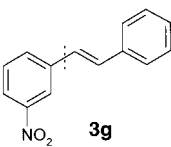
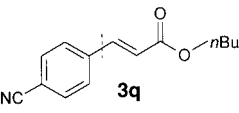
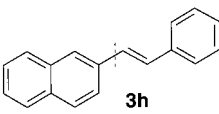
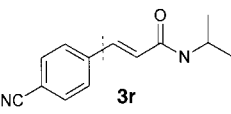
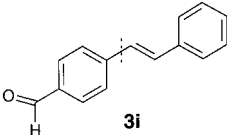
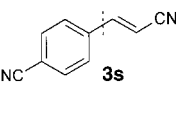
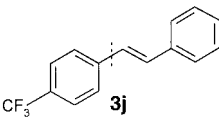
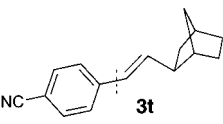
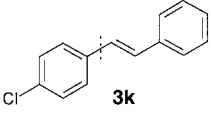
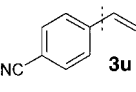
Various olefins are suitable substrates (**3q–u**). Both electron-rich and electron-poor olefins give similar yields. Even styrene derivatives are conveniently accessible in good yields when trimethylvinylsilane is used as an ethylene surrogate (**3u**).^[16] However, similarly to conventional Heck olefinations, the addition is not always completely regioselective; in some cases, Pd-catalyzed double-bond isomerization leads to the formation of complex product mixtures (**3q**).

In summary, the palladium-catalyzed Heck olefination disclosed herein represents a simple, high-yielding synthesis of functionalized vinyl arenes, heteroarenes, and 1,3-dienes from the plethora of available carboxylic acids via their nitrophenol esters. The nitrophenol esters are conveniently accessible from carboxylic acids and nitrophenol chloroformate. The alternative possibility of generating them directly from carboxylic acids and nitrophenol allows a low-waste reaction protocol for Heck olefinations. Further improvements of the catalytic system aiming at the conversion of esters of alkanols or phenol are under investigation in our research group.^[17]

Experimental Section

Synthesis of 1: A 50-mL flask was charged with the carboxylic acid (15 mmol), triethylamine (20 mmol), and dichloromethane (30 mL). Solid nitrophenyl chloroformate (3.02 g, 15 mmol) was added slowly, and the reaction mixture was stirred for a few minutes until gas evolution ceased. The reaction mixture was then filtered through a plug of basic aluminum oxide with dichloromethane as eluent. After recrystallization from hexane/

Table 3. Scope of the Heck olefination.

Product	Yield ^[a]	3/6 ^[b]	Product	Yield ^[a]	3/6 ^[b]
 3b	54 (60)	9:1	 3l	70 (85)	13:1
 3c	83 (99)	14:1	 3m	40 (60)	13:1
 3d	85 (99)	13:1	 3n	47 (53)	10:1
 3e	79 (96)	13:1	 3o	90 (98)	13:1
 3f	52 (53)	9:1	 3p	83 (83)	13:1
 3g	55 (60)	13:1	 3q	95 (99)	20:1
 3h	80 (85)	10:1	 3r	67 (90)	13:1
 3i	85 (98)	15:1	 3s	86 (98)	5:1
 3j	74 (98)	15:1	 3t	86 (92)	4:1 ^[c]
 3k	88 (95)	20:1	 3u	62 (64)	–

Conditions: nitrophenyl ester (1 mmol), olefin (1.2 mmol), PdCl₂ (0.03 mmol), LiCl (0.1 mmol), isoquinoline (0.3 mmol), NMP, 160 °C, 16 h. [a] Yields of isolated products (yields determined by GC are shown in parentheses). [b] The distribution of the isomers **3** and **6** was determined by GC analysis of the crude reaction mixture. [c] Mixture with small amounts of double-bond isomers.

ethyl acetate, the *p*-nitrophenyl benzoates were obtained as colorless crystals in excellent yields (85–95 %).

Synthesis of 1a from 5a: A 20-mL reaction flask was charged with nitrophenol (417 mg, 3 mmol), benzoic acid (244 mg, 2 mmol), and scandium triflate (29.5 mg, 0.06 mmol) and was fitted to a tube filled with molecular sieves (4 Å, 300 mg). The mixture was heated to 160 °C for 5 h. The progress of the reaction was monitored by GC. After the reaction was complete, the dark mixture was purified by Kugelrohr distillation to yield the desired nitrophenyl benzoate **1a** (398 mg, 82 %).

Synthesis of 3a–u: A 20-mL reaction vessel was charged with the nitrophenyl ester **1a–u** (1 mmol), PdCl₂ (5.3 mg, 0.03 mmol), LiCl (4.3 mg, 0.1 mmol), isoquinoline (38 mg, 0.3 mmol), and NMP (5 mL). The olefin **2a–f** (1.2 mmol) was then added through a syringe, and the reaction vessel was sealed with a septum. The reaction mixture was degassed by bubbling argon through the solution and was then slowly heated to 160 °C. The progress of the reaction was monitored by GC. When the reaction was complete (usually after 5 h), the reaction mixture was taken up in toluene and was washed sequentially with water, HCl (0.5 M), and aqueous sodium bicarbonate. The organic layer was dried over MgSO₄,

filtered, and the volatile components were removed in vacuo. The residue was isolated by means of column chromatography (SiO₂, dichloromethane:hexane 1:1–10:1) and characterized by means of ¹H and ¹³C NMR spectroscopy as well as by GC/MS and HRMS.

Received: January 4, 2002 [Z18481]

Electron-Hole Pairs Stabilized in Al-ZSM-5 Zeolites**



Alain Moissette,* Hervé Vezin, Isabelle Gener, Joël Patarin, and Claude Brémard

Photoinduced electron transfer to yield charged-separated states is the most fundamental energy conversion process of the photovoltaic effect, exciton storage in semiconductors, and photosynthesis. Ionization of organic molecules on heterogeneous catalysts^[1, 2] is predicted to become an exciting area of research. However, practical applications are often hampered by a rapid back reaction. Inhibition of the undesirable back-transfer of electrons requires control of both electronic and spatial properties of the system. Photoinduced charge separation can be achieved by sophisticated molecular triads and higher analogues that are currently capable of producing a charge-separated state with good yield and a lifetime of less than 1 s.^[3] Microporous aluminosilicate materials such as zeolites provide an appropriate micro-environment to efficiently trap electrons.^[4, 5] The electron trapped in zeolites can be generated in different ways: 1) radiolysis using high-energy radiations, 2) photolysis of preadsorbed molecules, and 3) mere exposure of electron-donor compounds such as alkali metal vapor or organic compounds to dehydrated zeolites. It appears that the presence of heteroatoms such as aluminum in the siliceous framework and extra-framework cations is a requirement for efficient electron trapping.^[6, 7] Although the characterization of occluded organic radical ions has been established, the whereabouts of electrons within the inorganic supports remains unclear and is the subject of considerable debate.^[1, 2, 4, 5, 8] Surprisingly, aluminosilicate zeolites are also known to contain electron-donor sites capable of transferring electrons to strong acceptors. Herein, we characterize the unusual system of acidic Al-ZSM-5 zeolite loaded with biphenyl (BP, C₁₂H₁₀) groups in which both electron-acceptor

- [1] a) R. F. Heck, *Org. React.* **1982**, 27–390; b) J. Tsuji, *Palladium Reagents and Catalysts—Innovations in Organic Synthesis*, Wiley, Chichester, UK, **1995**; c) A. de Meijere, F. E. Meyer, *Angew. Chem.* **1994**, 106, 2473–2506; *Angew. Chem. Int. Ed. Engl.* **1994**, 32, 2379–2411; d) N. J. Whitcombe, K. K. Hii, S. E. Gibson, *Tetrahedron* **2001**, 57, 7449–7476.
- [2] a) S. Cacchi, E. Moreau, G. Ortar, *Tetrahedron Lett.* **1984**, 25, 2271–2274; b) W. J. Scott, G. T. Crisp, J. K. Stille, *J. Am. Chem. Soc.* **1984**, 106, 4630–4632.
- [3] a) K. Kikukawa, T. Matsuda, *Chem. Lett.* **1977**, 159–162; b) K. Kikakuwa, K. Ikenaga, K. Kono, K. Toritani, F. Wada, T. Matsuda, *J. Organomet. Chem.* **1984**, 270, 277–282; c) M. Beller, H. Fischer, K. Kühlein, *Tetrahedron Lett.* **1994**, 35, 8773–8776.
- [4] M. Miura, H. Hashimoto, K. Itoh, M. Nomura, *J. Chem. Soc. Perkin Trans. I* **1990**, 8, 2207–2211.
- [5] a) H. U. Blaser, A. Spencer, *J. Organomet. Chem.* **1982**, 233, 267–274.
- [6] a) M. Portnoy, Y. Ben. David, I. Rouso, D. Milstein, *Organometallics* **1994**, 13, 3465–3479; b) W. A. Herrmann, C. Broßmer, K. Öfele, M. Beller, H. Fischer, *J. Mol. Catal. A* **1995**, 103, 133–146; c) K. H. Shaughnessy, P. Kim, J. F. Hartwig, *J. Am. Chem. Soc.* **1999**, 121, 2123–2132; d) A. F. Littke, G. C. Fu, *J. Org. Chem.* **1999**, 64, 10–11; e) A. Ehrentraut, A. Zapf, M. Beller, *Synlett* **2000**, 11, 1589–1592.
- [7] a) M. S. Stephan, A. J. J. M. Teunissen, G. K. M. Verzijl, J. G. de Vries, *Angew. Chem.* **1998**, 110, 688–690; *Angew. Chem. Int. Ed.* **1998**, 37, 662–664; b) A. F. Shmidt, V. V. Smirnov, *Kinet. Catal.* **2000**, 41, 743–744.
- [8] a) J. March, *Advanced Organic Chemistry*, Wiley, New York, 3rd ed., **1985**, p. 355; b) S. G. Burton, P. T. Kaye, *Synth. Commun.* **1989**, 19, 3331–3335.
- [9] For the application of coupling reagents in Pd catalysis, see: L. J. Gooßen, K. Ghosh, *Chem. Commun.* **2001**, 2084–2085.
- [10] C. Amatore, A. Jutand, *Acc. Chem. Res.* **2000**, 33, 314–321.
- [11] a) M. Itoh, *Chem. Pharm. Bull.* **1970**, 18, 784–788; b) J. Haeusler, U. Schmidt, *Chem. Ber.* **1974**, 107, 145–151.
- [12] T. Jeffery, *Tetrahedron* **1996**, 52, 10113–10130.
- [13] a) A. Spencer, *J. Organomet. Chem.* **1982**, 240, 209–216; b) C.-M. Andersson, A. Hallberg, *J. Org. Chem.* **1988**, 53, 235–239.
- [14] K. Nagayama, F. Kawataka, M. Sakamoto, I. Shimizu, A. Yamamoto, *Chem. Lett.* **1995**, 367–368; b) L. J. Gooßen, K. Ghosh, *Angew. Chem.* **2001**, 113, 3566; *Angew. Chem. Int. Ed.* **2001**, 40, 3458–3460.
- [15] a) J. March, *Advanced Organic Chemistry*, Wiley, New York, 3rd ed., **1985**, pp. 348–351; b) K. Ishihara, S. Ohara, H. Yamamoto, *Science* **2000**, 290, 1140–1142.
- [16] A. Hallberg, C. Westerlund, *Chem. Lett.* **1982**, 1993–1994.
- [17] L. J. Gooßen, J. Paetzold, patent application, **2001**.

[*] Dr. A. Moissette, Dr. C. Brémard

Laboratoire de Spectrochimie Infrarouge et Raman
UMR-CNRS 8516

Centre d'Etudes et de Recherches Lasers et Applications, Bât. C5
Université des Sciences et Technologies de Lille
59655 Villeneuve d'Ascq cedex (France)
Fax: (+33) 320-436-755
E-mail: alain.moissette@univ-lille1.fr

Dr. H. Vezin

Laboratoire de Chimie Organique et Macromoléculaire
ESA-CNRS 8009, Bât. C3

Université des Sciences et Technologies de Lille
59655, Villeneuve d'Ascq cedex (France)

Dr. I. Gener

Laboratoire de Catalyse en Chimie Organique, UMR-CNRS 6503
Université de Poitiers
40 avenue du recteur Pineau, 80022 Poitiers (France)

Dr. J. Patarin

Laboratoire des Matériaux Minéraux, ESA-CNRS 7016
Ecole Nationale Supérieure de Chimie de Mulhouse
3 rue Alfred Werner, 68093 Mulhouse cedex (France)

[**] The Centre d'Etudes et de Recherches Lasers et Applications (CERLA) is supported by the Ministère chargé de la recherche, the région Nord/Pas de Calais, and the Fonds Européen de Développement Economique des Régions.