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# A Survey of Palladium Catalyst Systems for Cross Coupling Reactions of Aryl Chlorides and Olefins

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## Abstract:

A detailed investigation into the influence of phosphines, additives, bases, and solvents on the *Heck* coupling reaction of 4-trifluoromethyl-1-chlorobenzene (**2**) is presented. It is shown that a number of catalyst systems exist for efficient cross coupling of electron deficient aryl chlorides with various olefins. Basicity and steric demand of the ligand are two factors which determine the success of the reaction. In addition the phosphine / palladium ratio, the correct type and amount of additive, and finally the use of an appropriate base and solvent are also important. The optimised reaction conditions are applied for the arylation of styrene, butyl vinyl ether, and *N,N*-dimethyl acrylic amide with various aryl chlorides.

## Introduction:

Among the various ways known to synthesise arylated olefins, probably the most powerful method is the construction of C(sp<sup>2</sup>)-C(sp<sup>2</sup>) single bonds through the palladium-catalysed coupling reactions of olefins with aryl halides (*Heck* reaction).<sup>[1]</sup> In general, aryl bromides, iodides, and triflates are used as starting materials for the *Heck* reaction. Due to the industrial importance of functionalising easily accessible and cheap aryl chlorides,<sup>[2]</sup> there is currently a great deal of interest in the coupling of aryl chlorides with various nucleophiles.<sup>[3]</sup> While J. Bozell<sup>[4]</sup> demonstrated that nickel / palladium mixtures promote effective coupling reactions with olefins, most studies have focussed on palladium catalysts. Although initial work conducted by W. A. Herrmann and us,<sup>[5]</sup> as well as D. Milstein,<sup>[6]</sup> and more recently by M. T. Reetz<sup>[7]</sup>, G. Fu,<sup>[8]</sup> and J. F. Hartwig<sup>[9]</sup> led to significant breakthroughs in this area, the factors affecting the efficiency of the coupling of aryl chlorides with olefins are far from being understood. It is generally accepted that certain recipes for “good” reaction conditions exist, but the exact influence of most reaction parameters remains unclear. In this full paper we report in detail the effect of additives, bases, and solvents on the catalytic performance of the palladacycle **1**, and of various palladium(II) acetate / phosphine *in situ* systems in the coupling reaction of 4-trifluoromethyl-1-chlorobenzene (**2**) and styrene (**3**). The optimised reaction conditions were applied to the *Heck* reaction of a variety of aryl chlorides and aryl bromides with different olefins.

## Results and Discussion:

Initially, we performed the coupling of 4-trifluoromethyl-1-chlorobenzene (**2**) and styrene (**3**) in the presence of palladacycle **1** as a model reaction (Scheme 1). Here, we studied the effect of added halide (cations and anions), bases, and the olefin concentration on catalyst productivity. All reactions were run at a low catalyst concentration (0.05 mol-

% **1** = 0.1 mol-% Pd). This is especially noteworthy because at this catalyst concentration no *Heck* reactions of aryl chlorides have been reported with traditional catalyst systems.

The negative inductive effect of the *para*-trifluoromethyl substituent leads to an activation of the C-Cl bond towards nucleophilic substitution.<sup>[10]</sup> Hence, 4-trifluoromethyl-1-chlorobenzene (**2**) should be viewed as a moderately activated aryl chloride for palladium-catalysed coupling reactions.

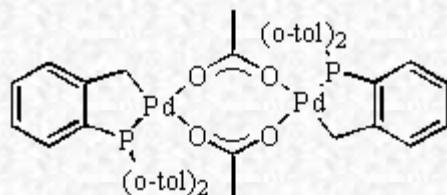
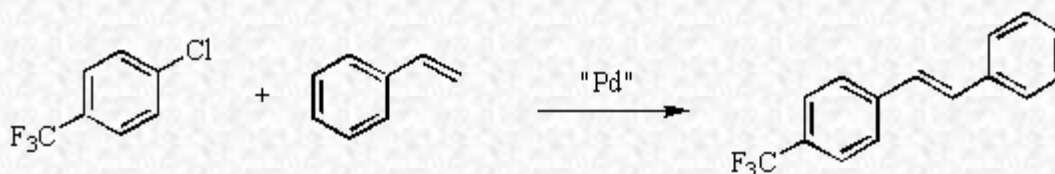


Figure 1. Palladacycle **1**.



Scheme 1. *Heck* reaction of 4-trifluoromethyl-1-chlorobenzene (**2**) and styrene (**3**).

In order to achieve significant conversion of chloroarenes in the palladacycle-catalysed *Heck* reaction comparatively high reaction temperatures (> 140 °C) are needed due to the relative stability of the C-Cl bond towards oxidative addition.<sup>[2a]</sup> Only the highly basic catalyst systems developed very recently do not need this thermal activation and allow *Heck* coupling of aryl chlorides at 100 - 120 °C.<sup>[6,8,9]</sup>

The palladacycle **1** is an ideal source for the slow generation of palladium monophosphine species, which are most likely the active catalytic species in the reaction mixture.<sup>[5e]</sup> In order to prevent deactivation (precipitation of palladium black) of these active species at higher reaction temperatures, it is necessary to add stabilising and/or activating agents to the reaction mixture. Soluble sources of bromide ions often show a beneficial effect in *Heck* reactions (Jeffery conditions).<sup>[1]</sup> Hence, we studied the influence of different concentrations of tetra-*n*-butylammonium bromide (TBAB) on the model reaction at 140 °C and 160 °C. Without any TBAB in the presence of 0.05 mol-% **1** and 1.2 equivalents of sodium acetate as the base only 2 % and 8 % of 4-trifluoromethyl stilbene (**4**) is formed after 20 h at 140 °C and 160 °C respectively. Increasing the halide concentration leads to an increased product yield at both temperatures. However, there are significant differences depending on the reaction temperature. As shown in Figure 2 at 160 °C the optimum concentration of TBAB lies at 20 mol-% relative to **2**, with 64 % of **4** being formed (TON = 640). At higher concentrations of TBAB the yield decreases, with only 10 % of **4** being obtained using 100 mol-% TBAB. We explain this decrease in product yield at higher concentrations of TBAB by the blocking of free coordination sites of low ligated palladium(0) complexes.

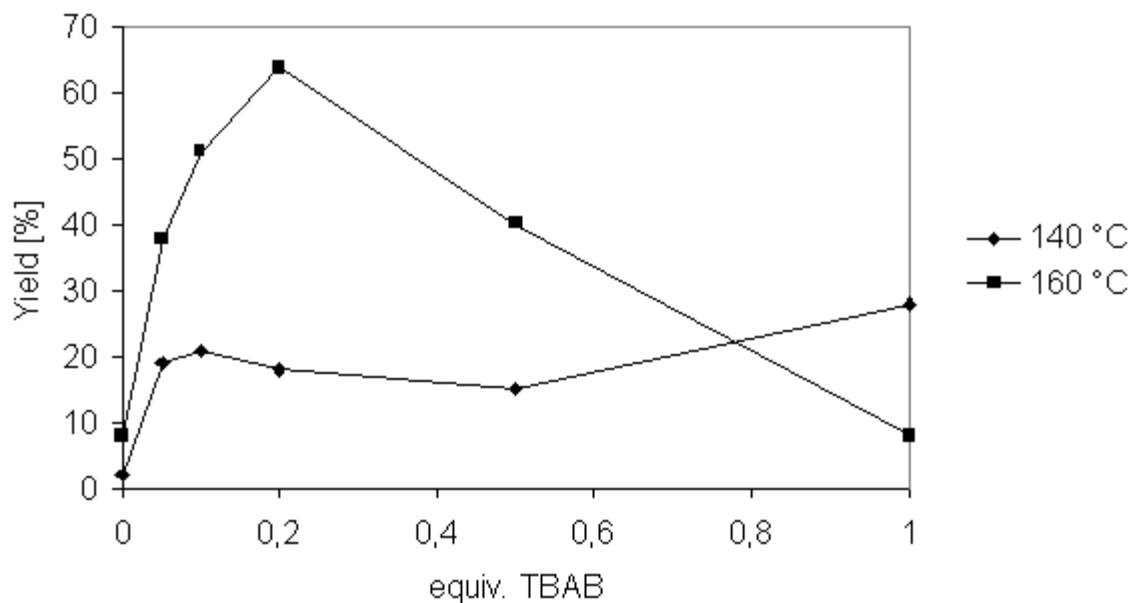
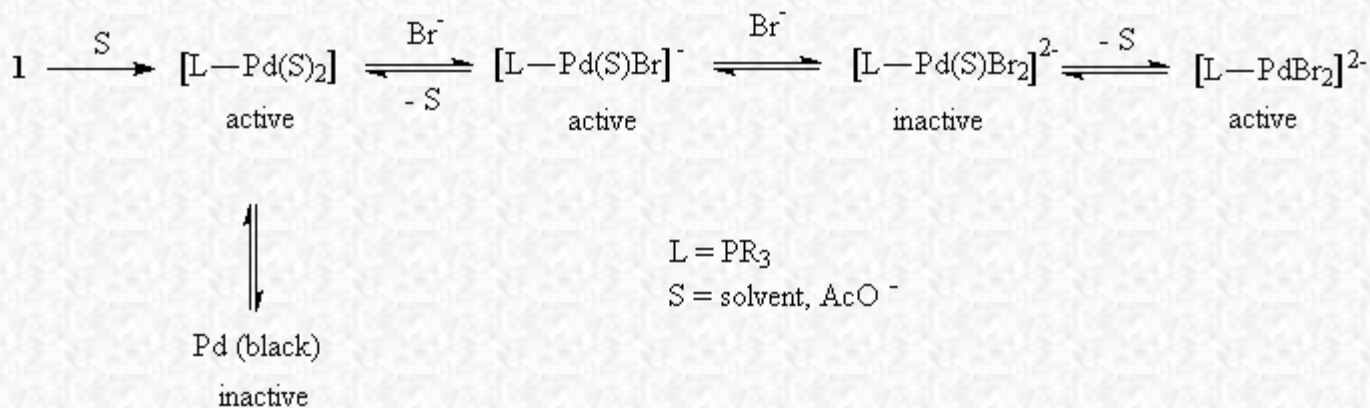


Figure 2. Effect of TBAB concentration (10 mmol 4-trifluoromethyl-1-chlorobenzene (**2**), 15 mmol styrene (**3**), 12 mmol sodium acetate, 0.005 mmol **1**, 10 ml DMAc, 20 h).

At 140 °C the yield of **4** is significantly lower compared to 160 °C, demonstrating that 140 °C is too low for an efficient activation of the substrate. After an initial increase in the yield by adding 5 mol-% of TBAB the halide concentration has only a marginal influence on the reaction outcome. Hence, **4** is obtained in 20 - 30 % yield in the presence of 5 - 100 mol-% TBAB. These results demonstrate that TBAB has both a positive and negative effect on the yield of **4** depending on the concentration and temperature. This can be explained by the fact that bromide ions facilitate the formation of anionic 14e- and 16e-Pd(0) monophosphine species (Scheme 2). At 160 °C the formation of these highly active species is fast and a higher halide concentration leads to the predominant formation of stable 18e-complexes. At 140 °C the conversion of **1** to anionic Pd(0) complexes is low, hence a higher halide concentration is beneficial for the initial step, but leads to less active, higher ligated species.



Scheme 2: Proposed equilibrium of Pd complexes.

While the initial catalyst tests were performed using sodium acetate as the base, we were also interested in the influence of other bases. Common bases for *Heck* reactions are the acetates, carbonates, and bicarbonates of alkaline or earth alkaline metals or alternatively organic bases such as trialkylamines.<sup>[1]</sup> Table 1 gives an overview of the results obtained in the presence of 1.2 equiv. of 11 different bases. Sodium and potassium acetate and sodium carbonate lead to similar results in the presence of 20 mol-% TBAB (64, 61, and 61 % of **4**, respectively). Silver acetate completely suppresses the catalytic activity (in the absence of TBAB). Soluble tetra-*n*-butylammonium acetate leads, without

added halide, to the formation of only 32 % of **4**. This is surprising because acetate ions should have a comparable stabilising effect on palladium(0) species due to *ate*-complex formation.<sup>[11]</sup> The expensive base caesium carbonate (25 %) as well as potassium phosphate (39 %) gave lower yields of **4**. Both potassium *tert*-butoxide and sodium hydroxide lead to catalyst decomposition under these conditions. Much to our surprise, simple calcium oxide, almost insoluble in the *N,N*-dimethyl acetamide (DMAc) solvent and to the best of our knowledge not used before in palladium-catalysed coupling reactions, performs excellently under these reaction conditions (67 % of **4**). Triethylamine is not suitable as base (12 % of **4**) due to its ability to bind strongly to palladium.

In all catalytic tests the selectivity for the *E*-isomer of **4** lies between 94 and 98 %, independent of the type of based used.

Table 1: Base effect on the coupling of 4-trifluoromethyl-1-chlorobenzene (**2**) and styrene (**3**).

Entry	Base	Bu <sub>4</sub> NBr [mol-%]	Yield [%] <sup>a)</sup>
<b>1</b>	<b>NaOAc</b>	<b>20</b>	<b>64</b>
<b>2</b>	<b>KOAc</b>	<b>20</b>	<b>61</b>
3	AgOAc	0	0
4	Bu <sub>4</sub> NOAc	0	32
<b>5</b>	<b>Na<sub>2</sub>CO<sub>3</sub></b>	<b>20</b>	<b>61</b>
6	Cs <sub>2</sub> CO <sub>3</sub>	20	25
7	K <sub>3</sub> PO <sub>4</sub>	20	39
8	KO <sup>t</sup> Bu	20	3
9	NaOH	20	4
<b>10</b>	<b>CaO</b>	<b>20</b>	<b>67</b>
11	NEt <sub>3</sub>	20	12

Reaction conditions: 10 mmol 4-trifluoromethyl-1-chlorobenzene (**2**), 15 mmol styrene (**3**), 12 mmol base, 2 mmol TBAB, 0.005 mmol **1**, 10 ml DMAc, 160 °C, 20 h; a) *E*-4-trifluoromethyl stilbene (**4**), determined by gas chromatography with diethyleneglycol di-*n*-butylether as the internal standard.

The ratio of aryl chloride to olefin is crucial for the outcome of the coupling reaction (Figure 3). A yield of 91 % of the desired stilbene **4** (relative to styrene) is observed by utilising 0.5 equiv. of styrene relative to **2**. Equimolar amounts of starting materials lead to a 66 % yield of **4**. A further increase in the styrene / aryl chloride ratio (1.5 - 5 equiv.) results in a continuous decrease in the product yield (64 - 23 %). Despite the lower yields, we decided to use 1 - 1.5 equiv. of the olefin in couplings of styrene on a preparative scale because this is the cheaper coupling partner compared to the aryl halide and it may oligo- or polymerise to some extent.

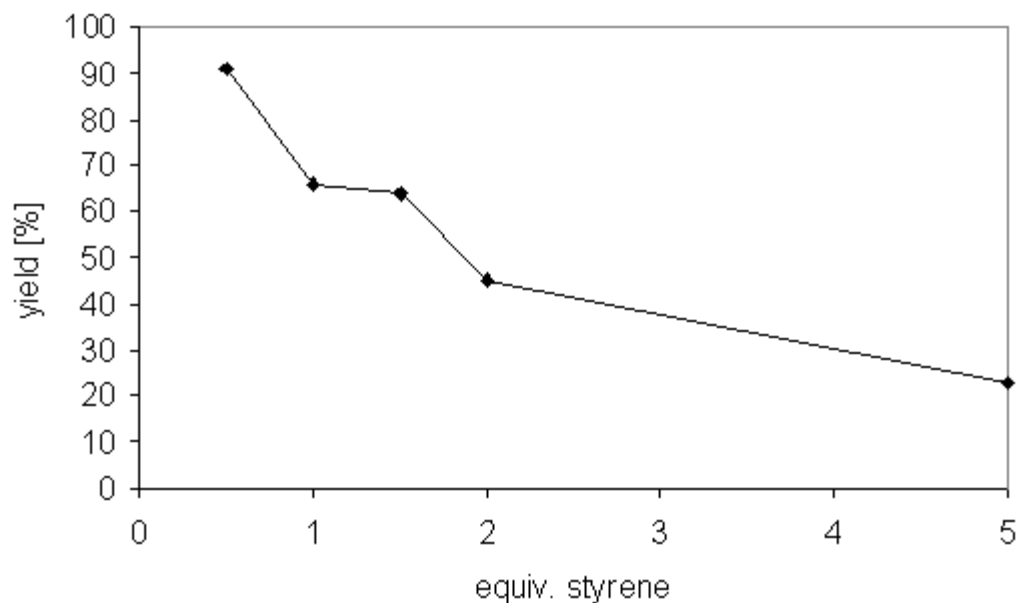


Figure 3. Influence of the styrene / aryl chloride ratio (10 mmol 4-trifluoromethyl-1-chlorobenzene (**2**), 2 mmol TBAB, 12 mmol sodium acetate, 0.005 mmol **1**, 10 ml DMAc, 160 °C, 20 h).

After considerable optimisation of the model reaction we were interested in the outcome of this coupling reaction in the presence of a series of halides and other co-ordinating and non co-ordinating salts. Investigations into the oxidative addition of aryl iodides to palladium(0) complexes confirm an activating and hence accelerating effect of added halide ions on this step of the catalytic cycle.<sup>[12]</sup> With regard to the results obtained with TBAB as the additive we believe that this is also valid for the coupling of aryl chlorides. Due to the fact that the addition of other anions (chloride,<sup>[13]</sup> iodide,<sup>[14]</sup> hydrogen sulfate,<sup>[15]</sup> acetate<sup>[16]</sup>) to palladium-catalysed coupling reactions is also beneficial in some cases, we tested various additives in the presence of sodium acetate and sodium carbonate (Tables 2 - 3). Table 2 gives a summary of the results observed in the presence of different tetra-*n*-butylammonium salts.

As can be seen from Table 2 tetra-*n*-butylammonium bromide (TBAB) is the most effective co-catalyst for this reaction if sodium acetate is used as the base. When sodium carbonate is utilised as the base, better results are obtained in the presence of tetra-*n*-butylammonium chloride hydrate (89 % of **4**), followed then by the corresponding bromide and hydrogen sulfate (61 and 58 % of **4**, respectively). By reaction with carbonate ions the latter additive can form hydroxide ions which are able to co-ordinate to palladium and hence lead to considerable stabilisation of the active species. The formation of hydroxide ions is probably also responsible for the beneficial effect of chloride and water compared to chloride without water. The basicity of acetate ions is not sufficient to deprotonate water to a reasonable extent. In this case, the combination of water and chloride has no significant positive influence on the catalytic efficiency. Weakly co-ordinating anions (acetate, nitrate) as well as non-coordinating anions (tetrafluoroborate, sulfonic acid anions) do not stabilise low ligated palladium(0) complexes towards agglomeration and hence do not allow reasonable conversion of the test substrate.

Table 2: Anion effect on the coupling of 4-trifluoromethyl-1-chlorobenzene (**2**) and styrene (**3**).

Entry	Cation	Anion	NaOAc		Na <sub>2</sub> CO <sub>3</sub>	
			Yield [%] <sup>a)</sup>	Sel. <i>E</i> [%]	Yield [%] <sup>a)</sup>	Sel. <i>E</i> [%]
1	Bu <sub>4</sub> N <sup>+</sup>	Cl <sup>-</sup>	21	97	29	98
<b>2</b>	<b>Bu<sub>4</sub>N<sup>+</sup></b>	<b>Cl<sup>-</sup> · H<sub>2</sub>O</b>	36	96	<b>89</b>	<b>95</b>

<b>3</b>	<b>Bu<sub>4</sub>N<sup>+</sup></b>	<b>Br<sup>-</sup></b>	<b>64</b>	<b>94</b>	<b>61</b>	<b>94</b>
4	Bu <sub>4</sub> N <sup>+</sup>	I <sup>-</sup>	35	91	11	94
5	Bu <sub>4</sub> N <sup>+</sup>	SCN <sup>-</sup> (20 mol-%)	1	nd <sup>b)</sup>		
6	Bu <sub>4</sub> N <sup>+</sup>	SCN <sup>-</sup> (0.1 mol-%)	1	nd		
7	Bu <sub>4</sub> N <sup>+</sup>	OAc <sup>-</sup>	34	95	43	95
8	Bu <sub>4</sub> N <sup>+</sup>	OH <sup>-</sup> (H <sub>2</sub> O sol.)	23	96	21	96
9	Bu <sub>4</sub> N <sup>+</sup>	OH <sup>-</sup> (MeOH sol.)	0	-	0	-
10	Bu <sub>4</sub> N <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	5	nd	9	nd
11	Bu <sub>4</sub> N <sup>+</sup>	HSO <sub>4</sub> <sup>-</sup>	16	97	<b>58</b>	<b>95</b>
12	Bu <sub>4</sub> N <sup>+</sup>	BF <sub>4</sub> <sup>-</sup>	2	nd		
13	Bu <sub>4</sub> N <sup>+</sup>	OTs <sup>-</sup>	4	nd		
14	Bu <sub>4</sub> N <sup>+</sup>	OTf <sup>-</sup>	1	nd		

Reaction conditions: 10 mmol 4-trifluoromethyl-1-chlorobenzene (**2**), 15 mmol styrene (**3**), 12 mmol base, 2 mmol additive, 0.005 mmol **1**, 10 ml DMAc, 160 °C, 20 h; a) *E*-4-trifluoromethyl stilbene (**4**), determined by gas chromatography with diethyleneglycol di-*n*-butylether as the internal standard; b) not determined.

During the investigations into the anion's influence on catalytic activity it became obvious that the cation might also have a significant impact on the success of the reaction. The results of screening different halide additives are summarised in Table 3. Readily soluble tetraalkylammonium and lithium bromides form the most active catalysts in combination with sodium acetate, while less soluble alkaline bromides lead to low conversions. Utilising sodium carbonate the *Hofmann* degradation of tetra-*n*-butylphosphonium bromide to form tri-*n*-butylphosphine, leading to an active catalyst system itself, predominates the effect of simply added bromide. The reasons for the different results combining tetra(*N,N*-diethylamino)phosphonium bromide with sodium acetate and carbonate, respectively, are not clear at the moment.

Table 3: Cation effect on the coupling of 4-trifluoromethyl-1-chlorobenzene (**2**) and styrene (**3**).

Entry	Cation	Anion	NaOAc		Na <sub>2</sub> CO <sub>3</sub>	
			Yield [%] <sup>a)</sup>	Sel. <i>E</i> [%]	Yield [%] <sup>a)</sup>	Sel. <i>E</i> [%]
1	Li <sup>+</sup>	Cl <sup>-</sup>	15	97	10	nd <sup>b)</sup>
3	Cs <sup>+</sup>	Cl <sup>-</sup>	8	nd	13	nd
4	Bu <sub>4</sub> N <sup>+</sup>	Cl <sup>-</sup>	21	97	29	98
<b>5</b>	<b>Bu<sub>4</sub>N<sup>+</sup></b>	<b>Cl<sup>-</sup> · H<sub>2</sub>O</b>	36	96	<b>89</b>	<b>95</b>
6	+	-	54	93	21	95



	Li	Br				
7	Na <sup>+</sup>	Br <sup>-</sup>	24	94	19	95
8	K <sup>+</sup>	Br <sup>-</sup>	29	94		
9	NH <sub>4</sub> <sup>+</sup>	Br <sup>-</sup>	22	95	28	96
10	Et <sub>4</sub> N <sup>+</sup>	Br <sup>-</sup>	31	95	30	97
<b>11</b>	<b>Bu<sub>4</sub>N<sup>+</sup></b>	<b>Br<sup>-</sup></b>	<b>64</b>	<b>94</b>	<b>61</b>	<b>94</b>
<b>12</b>	<b>Oc<sub>4</sub>N<sup>+</sup></b>	<b>Br<sup>-</sup></b>	56	93	<b>67</b>	<b>93</b>
<b>13</b>	<b>Bu<sub>4</sub>P<sup>+</sup></b>	<b>Br<sup>-</sup></b>	<b>60</b>	<b>93</b>	<b>90</b>	<b>93</b>
<b>14</b>	<b>(Et<sub>2</sub>N)<sub>4</sub>P<sup>+</sup></b>	<b>Br<sup>-</sup></b>	22	95	<b>85</b>	<b>94</b>
15	Me <sub>4</sub> N <sup>+</sup>	I <sup>-</sup>	39	90	8	94
16	Et <sub>4</sub> N <sup>+</sup>	I <sup>-</sup>	33	91	10	nd
17	Bu <sub>4</sub> N <sup>+</sup>	I <sup>-</sup>	35	91	11	94

Reaction conditions: 10 mmol 4-trifluoromethyl-1-chlorobenzene (**2**), 15 mmol styrene (**3**), 12 mmol base, 2 mmol additive, 0.005 mmol **1**, 10 ml DMAc, 160 °C, 20 h; a) *E*-trifluoromethyl stilbene (**4**), determined by gas chromatography with diethyleneglycol di-*n*-butylether as internal the standard; b) not determined.

At this time the cationic effect of additives seems to depend solely on their solubility. However, other ways of interacting with the substrate or the catalyst system can not be ruled out with certainty. NMR experiments to detect an interaction between the added cation and the chlorine of the aryl chloride were not successful. A change in the chemical shift of <sup>13</sup>C signal of the *ipso*-carbon atom could not be observed in DMAc/[d<sub>6</sub>]-DMSO (5:1) at room temperature ( $\delta = 137.2 - 137.6$  ppm). In addition, an influence of the cation on the chemical shift of triphenylphosphine / palladium(0) / bromide *ate*-complexes could also not be verified. In the <sup>31</sup>P NMR under “real” test conditions, albeit at room temperature, two signals were found for a mixture of Pd(PPh<sub>3</sub>)<sub>4</sub> / Br<sup>-</sup> / DMAc/[d<sub>6</sub>]-DMSO (5:1). Both signals were very broad and an assignment was difficult because the two signals represent a variety of both complexes and free phosphine which are all in fast equilibrium.

The additive did not significantly influence the geometry of the double bond formed (*E* vs. *Z*). In all cases 93 - 97 % of the *E*-isomer was obtained. However, iodide salts seem to decrease the selectivity marginally (*ca.* 91 % *E*) compared to the other anions investigated.

In the presence of 20 mol-% of transition metal halides as additives, *e. g.* manganese(II), cobalt(II), nickel(II), copper(I) or potassium trichlorostannate, no efficient conversion of **2** was observed (less than 20 % yield of **4**).

As shown in the experiments with tetra-*n*-butylammonium chloride and its hydrate, (Table 3, entries 4 - 5) added water may enhance the catalytic efficiency. In a series of experiments 0 - 1.0 equiv. of water was added at 160 °C in the presence of sodium carbonate. The optimum amount of water proved to be 0.5 equiv. in the presence of chloride ions. Less water does not activate the catalyst appreciably, and more than 1 equiv. of water leads to rapid palladium precipitation.

At this point three efficient catalyst systems based on the palladacycle **1** for the activation of **2** have been discovered.

In the presence of the economically attractive base sodium carbonate an 85 - 90 % yield (TON = 850 - 900) of **4** was realised applying either 0.2 equiv. tetra-*n*-butylphosphonium bromide, tetra(*N,N*-diethylamino)phosphonium bromide or tetra-*n*-butylammonium chloride hydrate.

Next, we were interested in a comparison of the molecularly defined complex **1** with traditional *in situ* catalyst systems. As stated previously palladium(II) / phosphine mixtures, which are generally applied for *Heck* and related reactions were not tested systematically for the activation of aryl chlorides at low catalyst loading (0.1 mol-% Pd) prior to our investigations. In order to observe positive as well as negative influences of the different commercially available phosphine ligands, we performed the model reaction under standard reaction conditions (DMAc, 160 °C, 20 h) with tetra-*n*-butylammonium bromide as the additive. Typically, phosphines are applied in palladium-catalysed coupling reactions in a molar ratio of 1:1 to 4:1 with respect to palladium. It is said that higher phosphine / palladium ratios slow down the coupling reaction.<sup>[18]</sup> Therefore we chose a P/Pd ratio of 2:1 for the phosphine screening. As shown in Table 4 most of the investigated ligands do not catalyse the test reaction to an appreciable extent with or without 20 mol-% of tetra-*n*-butylammonium bromide.

Table 4: Variation of phosphine ligands (P/Pd(OAc)<sub>2</sub> = 2:1) in the coupling of 4-trifluoromethyl-1-chlorobenzene (**2**) and styrene (**3**).

Entry	Phosphine	n [cm <sup>-1</sup> ] <sup>a)</sup>	Q [°] <sup>b)</sup>	Bu <sub>4</sub> NBr [mol-%]	Yield (Sel. <i>E</i> ) [%] <sup>c)</sup> (NaOAc)	Yield (Sel. <i>E</i> ) [%] <sup>c)</sup> (Na <sub>2</sub> CO <sub>3</sub> )
1	PCy <sub>3</sub>	2056	170	0	9	5
2	<b>PCy<sub>3</sub></b>	2056	170	20	<b>63 (94)</b>	39 (94)
3	<b>PBu<sub>3</sub></b>	2060	132	20	22 (96)	<b>83 (94)</b>
4	P[2,4,6-(MeO) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> ] <sub>3</sub>			20	18	3
5	P(NMe <sub>2</sub> ) <sub>3</sub>	2062	157	20	2	0
6	PMe <sub>2</sub> Ph	2065	122	20	13	7
8	dppb <sup>d)</sup>	2066		20	21 (96)	18 (96)
9	PmePh <sub>2</sub>	2067	136	20	22 (95)	14
11	PPh <sub>2</sub> (2-Py)			20	0	0
12	dppf <sup>e)</sup>			20	20	8
13	P( <i>o</i> -Tol) <sub>3</sub>	2067	194	20	0	1
14	BPT <sup>f)</sup>			20	18 (96)	13
15	PPh <sub>3</sub>	2069	145	20	1	7
16	P( <i>p</i> -C <sub>6</sub> H <sub>4</sub> -F) <sub>3</sub>	2071	145	20	0	2
17	P(CH <sub>2</sub> CH <sub>2</sub> CN) <sub>3</sub>	2078	132	20	3	10
18	P(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	2091	184	20	1	0



Reaction conditions: 10 mmol 4-trifluoromethyl-1-chlorobenzene (**2**), 15 mmol styrene (**3**), 12 mmol base, 0 or 2 mmol TBAB, 0.01 mmol palladium(II) acetate, 10 ml DMAc, 160 °C, 20 h; a)  $n_{\text{CO}}(A_1)$  of  $\text{Ni}(\text{CO})_3\text{L}$  in  $\text{CH}_2\text{Cl}_2$ ;[17] b) *Tolman* cone angle;[17] c) *E*-4-trifluoromethyl stilbene (**4**), determined by gas chromatography with diethyleneglycol di-*n*-butylether as the internal standard (selectivity of *E* isomer); d) 1,4-bis(diphenylphosphino)butane; e) 1,1'-bis(diphenylphosphino)ferrocene, f) 2,6-bis(diphenylphosphino)toluene.

In no case more than 10 % of desired stilbene **4** was formed in the absence of TBAB. Only two phosphines led to active catalyst systems under these conditions: tricyclohexylphosphine (63 % yield of **4** in the presence of sodium acetate) and tri-*n*-butylphosphine (83 % yield of **4** in the presence of sodium carbonate), which were the most basic ligands investigated in this study. However, basicity is not the only important factor determining the success of the reaction: tris(dimethylamino)phosphine which is only a bit less basic than tri-*n*-butylphosphine is not suitable for the model reaction at all. On the other hand steric effects are also not the sole determining factor, e. g. tricyclohexylphosphine and tri-*n*-butylphosphine work almost equally well. More electron poor ligands whose size is comparable to the former [tris(perfluorophenyl)phosphine] or the latter [tris(2-cyanoethyl)phosphine] ligand do not support the reaction (< 10 % yield of **4**). Surprisingly, tri-*o*-tolylphosphine does not lead to an active catalyst system when applied *in situ*. Palladium precipitation occurs faster compared to complexation and concomitant cyclometallation. Similarly to the palladacycle catalyst **1** the selectivity towards the *E* double bond isomer is between 94 and 96 % in all cases.

In contrast to catalyst **1** the formation of palladium black is observed in numerous reactions. Hence, we assumed that the stabilisation of the active palladium species by a slight excess of ligand (2:1) is not sufficient. Therefore the dependence of catalyst productivity on the phosphine / palladium ratio was investigated.

As shown in Figure 4 the coupling of 4-trifluoromethyl-1-chlorobenzene (**2**) with styrene (**3**) can be affected by means of simple triphenylphosphine if the ligand is provided in an excess relative to palladium. The best yield of **4** (72 %) is observed at a phosphine / palladium ratio of 15:1 in the presence of tetra-*n*-butylammonium bromide.

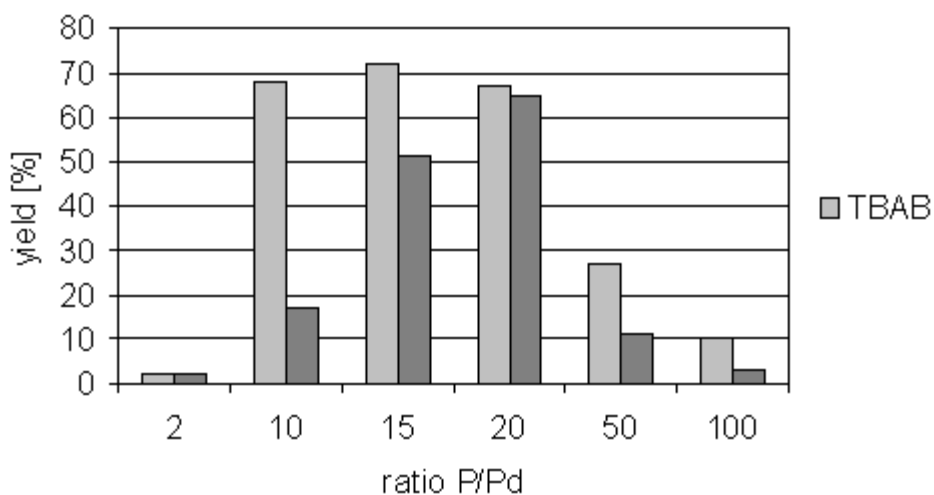


Figure 4. Influence of the P / Pd ratio (10 mmol 4-trifluoromethyl-1-chlorobenzene (**2**), 15 mmol styrene (**3**), 0 or 2 mmol TBAB, 12 mmol sodium acetate, 0.01 mmol palladium(II) acetate, 10 ml DMAc, 160 °C, 20 h).

If the co-catalyst is omitted comparable results (65 %) are obtained at a slightly higher molar ratio of phosphine to palladium (20:1). Higher concentrations of phosphine ligand lead to a decrease in catalyst activity, although the catalyst is stabilised against decomposition. Interestingly, increasing the phosphine / palladium ratio results in a significant decrease of *E* selectivity in the coupling product (P / Pd = 10:1, *E*-selectivity of **4** = 91 %; P / Pd = 100:1, *E*-selectivity of **4** = 79 %).

Table 5: Variation of phosphine ligands (P / Pd(OAc)<sub>2</sub> = 10:1) in the coupling of 4-trifluoromethyl-1-chlorobenzene (**2**) and styrene (**3**).

Entry	Phosphine	Bu <sub>4</sub> NBr [mol-%]	Yield [%] <sup>a)</sup>	Sel. <i>E</i> [%]
1	PCy <sub>3</sub>	0	40	92
<b>2</b>	<b>PCy<sub>3</sub></b>	<b>20</b>	<b>72</b>	<b>92</b>
3	PBu <sub>3</sub>	0	0	-
4	PBu <sub>3</sub>	20	0	-
5	P[2,4,6-(MeO) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> ] <sub>3</sub>	20	31	94
6	dppb <sup>b)</sup>	20	55	90
7	PMePh <sub>2</sub>	20	19	87
8	PAllPh <sub>2</sub>	20	50	92
9	dppf <sup>c)</sup>	20	43	92
10	P(CH <sub>2</sub> CH <sub>2</sub> CN) <sub>3</sub>	20	17	90

Reaction conditions: 10 mmol 4-trifluoromethyl-1-chlorobenzene (**2**), 15 mmol styrene (**3**), 12 mmol sodium acetate, 0 or 2 mmol TBAB, 0.01 mmol palladium(II) acetate, 10 ml DMAc, 160 °C, 20 h; a) *E*-4-trifluoromethyl stilbene (**4**), determined by gas chromatography with diethyleneglycol di-*n*-butylether as the internal standard (selectivity of *E* isomer); b) 1,4-bis(diphenylphosphino)butane; c) 1,1'-bis(diphenylphosphino)ferrocene.

The success in coupling our test substrates in the presence of an excess of triphenylphosphine prompted us to re-investigate the ligand influence at higher phosphine / palladium ratios (Table 5). All reactions resulted in significantly higher product yields when a 10-fold excess of ligand is applied compared to the initial 2-fold excess. The only exception was tri-*n*-butylphosphine which led to 53 % of **4** compared to 83 % at lower phosphine / palladium ratio.

Some important conclusions can be drawn from these results: 1. Regardless of the phosphine ligand employed, substantial yields of *Heck* products can be obtained even in the olefination of chloroarenes, if just the optimal conditions with respect to P / Pd ratio, base, and co-catalyst are used. 2. An important but generally overlooked reaction parameter is the ligand / palladium ratio. 3. The combination of the right ligand / palladium ratio and the reaction temperature allows an efficient activation of C-Cl bonds at low catalyst loading.

Remarkably, even catalyst systems comprising of electron poor phosphite ligands efficiently catalyse the *Heck* coupling of chloroarenes with various olefins, if the ligand is provided in an excess.<sup>[19]</sup>

The last reaction parameter studied in the model reaction was the influence of the solvent. *Heck* reactions are normally conducted in dipolar aprotic solvents like DMAc, DMF or acetonitrile. Therefore we investigated different polar solvents such as *N,N,N',N'*-tetramethylurea (TMU), NMP, DMAc, polyethylene glycol, and ethylene glycol in the presence of the most economically attractive catalyst system [Pd(OAc)<sub>2</sub> / 15 PPh<sub>3</sub>]. Independent of the base used, NMP gave slightly better results compared to DMAc and TMU.

Table 6: Coupling of 4-trifluoromethyl-1-chlorobenzene (**2**) and styrene (**3**) in polar solvents.

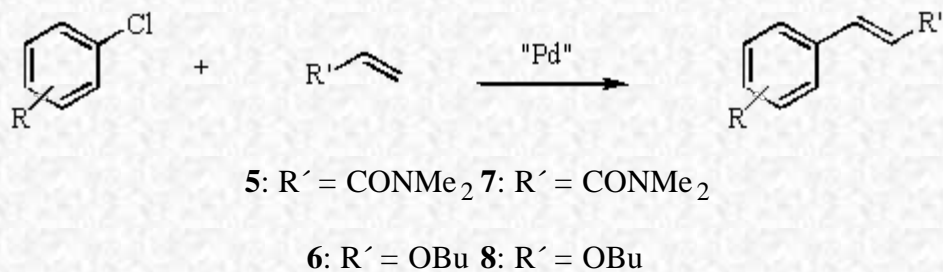
Entry	Solvent	Yield [%] <sup>a)</sup> (dehal.)	Yield [%] <sup>a)</sup> (dehal.)
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		NaOAc	Na <sub>2</sub> CO <sub>3</sub>
1	DMAc	56	40
2	<b>NMP</b>	<b>63</b>	<b>59</b>
3	TMU <sup>b)</sup>	48	48
4	PEG 400 <sup>c)</sup>	25 (10)	2 (37)
5	ethylene glycol	11 (28)	2 (32)

Reaction conditions: 10 mmol 4-trifluoromethyl-1-chlorobenzene (**2**), 15 mmol styrene (**3**), 12 mmol base, 0.01 mmol palladium(II) acetate, 0.15 mmol triphenylphosphine, 9 ml solvent, 1 ml toluene, 160 °C, 20 h; a) *E*-4-trifluoromethyl stilbene (**4**), determined by gas chromatography with diethyleneglycol di-*n*-butylether as the internal standard (yield of trifluoromethylbenzene); b) *N,N,N',N'*-tetramethylurea; c) polyethylene glycol 400.

In ethylene glycol and polyethylene glycol 400 rapid palladium decomposition takes place, thus these solvents do not allow an efficient coupling of **2** and **3**. Reductive dehalogenation of **2** to trifluoromethylbenzene is observed as a major side reaction (37 %).

The studies of the model reaction reveal that there are more than 12 different combinations of palladium source, co-catalyst (halide), base, and P / Pd ratio which are able to catalyse the coupling of **2** and **3** in yields from 60 - 90 % at a low catalyst loading. Nine of these “best” catalyst systems were chosen and applied to the *Heck* reaction of **2** and *N,N*-dimethyl acrylic amide and *n*-butyl vinyl ether (Scheme 3; Table 7).



Scheme 3. Coupling of aryl chlorides and olefins in the presence of different catalyst systems.

Table 7: Coupling of 4-trifluoromethyl-1-chlorobenzene (**2**) with different olefins (R = 4-CF<sub>3</sub>).

Entry	Cat.	Bu <sub>4</sub> NBr [mol-%]	Base	Yield [%] <sup>a)</sup> R' = Ph	Yield [%] <sup>a)</sup> R' = CONMe <sub>2</sub>	Conversion [%] <sup>a)</sup> R' = OBu
1	<b>1</b>	20	NaOAc	64	44	3
2	<b>1</b>	b)	Na <sub>2</sub> CO <sub>3</sub>	69	31	20
3	<b>Pd(OAc)<sub>2</sub></b> <b>20 PPh<sub>3</sub></b>	<b>0</b>	<b>NaOAc</b>	<b>65</b>	<b>60</b>	<b>90</b>
4	<b>Pd(OAc)<sub>2</sub></b> <b>15 PPh<sub>3</sub></b>	<b>20</b>	<b>NaOAc</b>	<b>72</b>	<b>56</b>	<b>nd</b>

5	Pd(OAc) <sub>2</sub> 5 dpbb	20	NaOAc	55	44	29
<b>6</b>	<b>Pd(OAc)<sub>2</sub></b> <b>10 PCy<sub>3</sub></b>	<b>20</b>	<b>NaOAc</b>	<b>72</b>	<b>56</b>	<b>92</b>
7	Pd(OAc) <sub>2</sub> 2 PBu <sub>3</sub>	20	Na <sub>2</sub> CO <sub>3</sub>	83	8	43
8	Pd(OAc) <sub>2</sub> 100 P(OEt) <sub>3</sub>	20	Na <sub>2</sub> CO <sub>3</sub>	71	13	62
<b>9</b>	<b>Pd(OAc)<sub>2</sub></b> <b>10</b> <b>P(OAr)<sub>3</sub><sup>c)</sup></b>	<b>20</b>	<b>Na<sub>2</sub>CO<sub>3</sub></b>	<b>90</b>	<b>89</b>	<b>nd</b>

Reaction conditions: 10 mmol 4-trifluoromethyl-1-chlorobenzene (**2**), 15 mmol olefin, 12 mmol base, 0.01 mmol catalyst, 10 ml DMAc, 160 °C, 24 h; a) yield *E*-product (conversion, respectively) determined by gas chromatography with diethyleneglycol di-*n*-butylether as the internal standard; b) 20 mol-% Bu<sub>4</sub>NCl, 50 mol-% H<sub>2</sub>O; c) Ar = 2,6-di-*t*-butylphenyl.

With the exception of the palladium(II) / phosphite catalyst system (89 % of **7**) and the palladium(II) / 20 triphenylphosphine catalyst (60 % of **7**) the coupling of *N,N*-dimethyl acrylic amide proceeds in significant lower yields compared to the coupling reaction with styrene. In addition, palladium(II) / 15 triphenylphosphine and palladium(II) / 10 tricyclohexylphosphine, both in the presence of TBAB, gave a substantial yield of product **7** (56 %). The reaction of **2** and **6** leads mainly to *n*-butoxy-4-trifluoromethyl styrene **8**. Obviously, no clear trend between catalyst system and product yield exists. Excellent conversions (90 - 92 %) to yield **8** were obtained with palladium(II) / 20 triphenylphosphine and palladium(II) / 10 tricyclohexylphosphine with 20 mol-% TBAB. Most other catalyst systems gave **8** only in low yields.

Next, selected *Heck* reactions of **3**, **5**, and **6** with 3-trifluoromethyl-1-chlorobenzene (**9**), chlorobenzene (**10**), 4-chloroanisole (**11**), and 4-chloroacetophenone (**12**) were performed. Olefination of **9** occurs with similar or lower yields compared to the reactions of the more activated *p*-isomer (Table 8). Again the best catalyst systems are *in situ* mixtures of palladium(II) and an excess of triphenylphosphine, tricyclohexylphosphine or triarylphosphite. The best product yields (67 - 93 %) were obtained with styrene, while *N,N*-dimethyl acrylic amide and *n*-butyl vinyl ether gave yields up to 63 % and 54 % respectively. The reaction of **12** with styrene in the presence of palladium(II) / 15 triphenylphosphine proceeds in good yield (60 %), due to the activating nature of the substituent.

Table 8: Coupling of 3-trifluoromethyl-1-chlorobenzene (**9**) with different olefins (R = 3-CF<sub>3</sub>).

Entry	Cat.	Bu <sub>4</sub> NBr [mol-%]	Base	Yield [%] <sup>a)</sup> R' = Ph	Yield [%] <sup>a)</sup> R' = CONMe <sub>2</sub>	Conversion [%] <sup>a)</sup> R' = Obu
1	<b>1</b>	20	NaOAc	52	19	0

2	<b>1</b>	b)	Na <sub>2</sub> CO <sub>3</sub>	55	41	0
3	Pd(OAc) <sub>2</sub> 20 PPh <sub>3</sub>	0	NaOAc	7	20	34
<b>4</b>	<b>Pd(OAc)<sub>2</sub></b> <b>15 PPh<sub>3</sub></b>	<b>20</b>	<b>NaOAc</b>	<b>67</b>	<b>53</b>	<b>47</b>
5	Pd(OAc) <sub>2</sub> 5 dppb	20	NaOAc	35	35	20
<b>6</b>	<b>Pd(OAc)<sub>2</sub></b> <b>10 PCy<sub>3</sub></b>	<b>20</b>	<b>NaOAc</b>	<b>85</b>	<b>36</b>	<b>64</b>
7	Pd(OAc) <sub>2</sub> 2 PBu <sub>3</sub>	20	Na <sub>2</sub> CO <sub>3</sub>	71	36	0
8	Pd(OAc) <sub>2</sub> 100 P(OEt) <sub>3</sub>	20	Na <sub>2</sub> CO <sub>3</sub>	79	12	59
<b>9</b>	<b>Pd(OAc)<sub>2</sub></b> <b>10</b> <b>P(OAr)<sub>3</sub><sup>c)</sup></b>	<b>20</b>	<b>Na<sub>2</sub>CO<sub>3</sub></b>	<b>93</b>	<b>42</b>	<b>nd</b>

10 mmol 3-trifluoromethyl-1-chlorobenzene (**9**), 15 mmol olefin, 12 mmol base, 0.01 mmol catalyst, 10 ml DMAc, 160 °C, 24 h; a) yield *E*-product (conversion, respectively) determined by gas chromatography with diethyleneglycol di-*n*-butylether as internal standard; b) 20 mol-% Bu<sub>4</sub>NCl, 50 mol-% H<sub>2</sub>O; c) Ar = 2,6-di-*t*-butylphenyl.

Utilising chlorobenzene as the substrate never gave more than 13 % of stilbene. Analogously, *N,N*-dimethyl cinnamic amide could hardly be detected in the coupling reaction (< 5 % yield). Reaction of 4-chloroanisole with styrene resulted in 17 % of 4-methoxy stilbene in the presence of palladium(II) acetate / 20 triphenylphosphine. All other catalyst systems under investigation led to less than 5 % of the corresponding coupling product. Although the yields of the *Heck* reaction of non-activated aryl chlorides are not sufficient for organic synthesis, the achieved turnover numbers of 130 - 170 are remarkable from a catalytic point of view.

### Conclusion:

What can we learn from this study of various catalyst systems for the *Heck* reaction of activated and non-activated aryl chlorides and olefins? Firstly, for activated aryl chlorides a number of useful catalyst systems exist, which allow these reactions to proceed in good to excellent yield with catalyst turnover numbers of *ca.* 1000. The industrial realisation in the area of fine chemicals is nowadays, in our opinion, feasible. Importantly, the outcome of the many possible combinations of phosphine / additive / base is not easily predicted. While some general guidelines exist, *e. g.* to use a higher P / Pd ratio, small changes in the co-catalyst or base may lead to a dramatic decrease in catalyst productivity. Contrary to traditional belief, basicity or steric demand of the ligand is not decisive for the success of the reaction under our conditions. Here, the phosphine / palladium ratio and the olefin concentration seem to be more important.

In addition, one must note that the reaction conditions once optimised for a special pair of coupling partners are not automatically suitable for a similar coupling reaction. Slight changes in the substrate may have a dramatic effect on the reaction outcome. Unfortunately, this means that every substrate combination needs its own optimisation protocol.

With regard to the *Heck* coupling of non-activated aryl chlorides, more efficient catalyst systems are badly needed. Although the catalyst productivity of the simple Pd / excess PPh<sub>3</sub> catalysts presented here is in the range of 100 - 200, product yields are low. However, even the new basic and sterically demanding ligands such as tri-*tert*-butylphosphine<sup>[8]</sup> or the new adamantylphosphines<sup>[3q,20]</sup> allow the reaction to proceed in good yield only at a comparable high catalyst concentration.

### Experimental Section:

**General:** All chemicals were commercially available and used without further purification. DMAc was distilled over calcium hydride and stored under argon. The coupling products synthesised were characterised using GC/MS, <sup>1</sup>H- and <sup>13</sup>C-NMR.

**General procedure:** In an ACE pressure tube (Aldrich) 10 mmol aryl halide, 15 mmol olefin, 12 mmol base, 400 mg diethyleneglycol di-*n*-butylether (as the internal standard), an appropriate amount of additive (if necessary), ligand, and palladium source is suspended in 10 ml of dry DMAc under an atmosphere of argon. The tube is sealed and put in a preheated bath of silicon oil. After 20 h the mixture is cooled to room temperature and 10 ml CH<sub>2</sub>Cl<sub>2</sub> and 10 ml of 2 *N* HCl are added. The organic phase is analysed by gas chromatography. After washing the organic phase with water and brine, drying and evaporating the solvents, the products are isolated by crystallisation from methanol / acetone mixtures or by column chromatography (silica gel, hexane / ethyl acetate mixtures).

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