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Heck reaction catalyzed by Pd/C, in a triphasic—organic/Aliquat 336/aqueous—solvent system

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The rate of the Pd/C catalyzed Heck coupling of Ar-I with $CH_2{=}CH\text{-}R$ is accelerated tenfold by the presence of Aliquat 336 (A336), a well known phase transfer catalyst, and an ionic liquid. Both when conducted in A336 as solvent, and in an isooctane/A336/aqueous triphasic mixture, the Heck reaction of aryl iodides with electron deficient olefins, catalyzed by Pd/C, proceeds with high yields and selectivity. When KOH is used instead of Et_3N, selective formation of the biphenyl rather than the Heck product, is observed. Aryl bromides react more sluggishly, and only the more activated ones undergo the Heck reaction. In the absence of the olefin, aryl halides possessing an electron withdrawing group are reduced to the corresponding Ar-H.

Introduction

The Heck reaction has been widely investigated using, in the majority of cases, a soluble metal complex as the catalyst. Traditional homogeneous catalysis is very efficient, but requires the use of solvents (usually organic), the catalyst may need to be complexed/activated by ligands such as phosphines, catalysts must often be synthesized, separated from the product, and regenerated at the end.[1] The latter drawback has been addressed in a number of ways, the most obvious being the use of heterogeneous catalysts or of systems where the catalyst is immobilized in a separate phase.

Heterogeneous catalysis

Reports on the heterogeneously catalyzed Heck reaction include the use of Pd/C as catalyst;[2–4] of Pd/SiO_2;[3,4] of Pd–Cu exchanged clays;[5] of palladium grafted on silica;[6,7] of a Pd–phosphine catalyst immobilized in an ethylene glycol film on a silica support;[8] of basic zeolites containing Pd[9] and of polymer supported catalysts.[10,11] In some cases it was noted that the active Pd species leached into the bulk of the solution[3,4] or that NMP had to be used as a solvent,[2–4] in others the catalysts were developed and prepared *ad hoc*.[5–10] The commonly studied reaction was that of iodobenzenes and acrylates, to give the corresponding cinnamate. Yields were good in most cases, at temperatures between 75 and 140 °C. The heterogeneous Heck coupling of aryl chlorides, using a Pd containing silico aluminophosphate-31, was also achieved, at 120 °C in DMA as solvent.[12]

Homogeneous catalyst immobilized in ionic liquids

Another solution to the problems of product–catalyst separation, and of catalyst recovery and regeneration, consists in running the reaction using a catalyst–solvent system where the homogeneous catalyst is dissolved in a liquid that (a) allows easy recovery of the products (and by-products), and (b) to reuse the catalyst–solvent ensemble. This can be achieved by using a solvent with a negligible vapour pressure—where the catalyst remains segregated—and from which the products can be recovered either by distillation, or extraction, or phase separation. The solvent can be for example a PEG[13] or an ionic liquid. Molten salts were shown to be good media for the Heck reaction as early as 1996, and Pd appeared to be stabilized under these conditions.[14] After that report, others have investigated the field.[15,16]

An elegant extension was reported by Earle, Seddon and co-workers with the use of a triphasic system constituted by an ionic liquid phase containing the Pd catalyst, a water layer used to scavenge inorganic byproducts, and an organic phase that contained the reagents and products; product–byproduct–catalyst separation could be achieved taking advantage of this triple phase separation.[17] The Heck reaction between aryl iodides and activated olefins was reported in the ionic liquid [bmim]PF_6 with a Pd/C catalyst as well.[18]

Jeffery also noted that the Heck reaction was favoured by phase transfer catalysts (PTC), such as quaternary ammonium salts.[19,20]

It therefore appears that the Heck reaction benefits from the presence of a PTC, *either in the form of a* PTC *or of an* ionic liquid.

This paper describes the Pd/C catalyzed Heck reaction conducted in the multiphase (isooctane/water) system, in the presence of Aliquat 336 (tricaprylmethylammonium chloride, A336), a liquid PTC. The system is in effect triphasic because when water is added to an isooctane solution of A336 a third liquid phase of A336 separates out. When the Pd/C catalyst is added, it goes all to the A336 phase. A336 can be added in catalytic amounts as well. In this case, due to the small volume of A336, the third liquid phase embodies the Pd/C, and the catalyst–A336 ensemble settles at the organic–aqueous interface. This catalytic system was developed, in particular, because it promotes the hydrodehalogenation of aryl halides under mild conditions in the liquid phase (50 °C, and atmospheric pressure of hydrogen).[21–26] The A336 layer was shown to modify catalyst properties such as selectivity and kinetics.[27–30]

Since this system is highly active and selective for the activation of aryl halides, the goal was to establish whether the presence of A336 promotes the heterogeneous Heck reaction as well. Next, to test it in the multiphase system made by the aqueous/organic solvents, and the heterogeneous catalyst suspended in the A336 phase. Further, to determine the reactivity of different substrates (aryl halides and olefins), and the effect of different bases.

Results and discussion

1 Effect of A336

A screening was done to determine the effect of A336 on the Pd/C catalyzed coupling reaction of phenyl iodide **1a** and ethyl acrylate **2a** to yield the Heck product, *trans*-ethyl cinnamate (**3a**), in the presence of Et_3N [eqn. (1)]. A mixture of PhI (1 mmol), ethyl acrylate (1.5 mmol), 5% Pd/C (0.05 mmol Pd), Et_3N (1.5 mmol), and 10 mL of the indicated solvent, was heated at 100 °C under a nitrogen atmosphere. Aliquat 336, was added in a catalytic amount (0.3 mmol), and in one case was used as solvent (3 mL). The results are collected in Table 1, where conversion and yields of each reaction are compared after 1.5 h. No products other than *trans*-ethyl cinnamate **3a** were detected.

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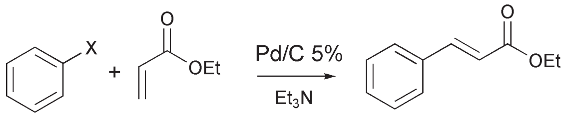
Table 1 Effect of A336 on the Heck coupling reaction [eqn. (1)][a]

Entry	X	Solvent	A336	Time/h	**3a** (%GC)
1	I	None	No	1.5	50
				4.0	100
2	I	A336 (3 mL)	Yes	0.3	100
3	I	*i*-Octane	No	1.5	10
4	I	*i*-Octane	Yes	1.5	50
5	I	Water	No	1.5	17
				5.5	40
6	I	Water	Yes	1.5	68
				5.5	82
7	Br	A336 (3 mL)	Yes	1.5	55
				3.5	100

[a] Reaction conditions: $T = 100$ °C, N_2 atmosphere, Pd/C 5% catalyst (0.05% mmol Pd), PhX (1.0 mmol), ethyl acrylate (1.5 mmol), Et_3N (1.5 mmol), A336 (0.3 mmol), 10 mL solvent.



1a: X = I **2a** **3a**
1b: X = Br (1)

The solventless reaction proceeded to a 100% yield of **3a** after 4 hours (entry 1). When A336 was used as a solvent, complete conversion was reached already after 20 min (entry 2).

Two different solvents, water and isooctane, were explored.

In the presence of catalytic amounts of A336, after 1.5 h, 50 and 68% yield of **3a** was obtained using isooctane (entry 4) and water (entry 6), respectively. In its absence the reaction slowed remarkably with both solvents: 10% and 17% yield of **3a** was obtained using isooctane (entry 3) and water (entry 5), respectively.

Using PhBr **1b** the Heck reaction in A336 as solvent was complete after 3.5 h at 100 °C (entry 7). With PhCl it was practically inhibited (not in table).

In all cases, a beneficial effect of A336 on the rate of the Heck reaction was observed, in analogy to the behaviour already observed for other PTCs.[14–20]

Multiphase conditions. The effect of A336 on the Heck coupling was then investigated in the multiphase system. A series of reactions was run using different substituted iodobenzenes and different olefins, a commercial Pd/C catalyst suspended in two immiscible phases (water and isooctane), and in the presence of triethylamine. Along with the Heck product (**3**), the Ullmann coupling product (**4**), and the reduced Ar-H (**5**), were sometimes observed [eqn. (2)]. The results are shown in Table 2.

In the multiphase system, the Heck coupling of iodobenzene **1a** with ethyl acrylate **2a** was favoured by the presence of A336. After 20 h, complete conversion was observed and **3a** was obtained in 94% yield, with only small amounts of Ullmann type coupling (biphenyl **4a** <6%, entry 2). Without A336 the reaction was sluggish, and a 15% yield of cinnamate **3a** was reached after 20 hours (entry 1).

In order to investigate the influence of different substituents, *p*-methoxy- (**1c**), *p*-nitro (**1d**), *p*-amino- (**1e**), *p*-chloro- (**1f**), *p*-MeCO- (**1g**), and *m*-cyano- (**1h**) substituted iodobenzenes were made to react with **2a**, and in the presence of A336 and Et_3N. The reactivity scale was the following.

Table 2 Multiphase Heck coupling of Z-C_6H_4-I with ethyl acrylate [eqn. (2)][a]

					Products (% GC)		
Entry	Z	A336	Time/h	Conv. (%)	**3**	**4**	**5**
1	H	No	1.5	5	5	0	0
			20	17	17		
2	H	Yes	1.5	30	30	0	0
			20	100	94	6	
3	*p*-NO_2	No[b]	6.0	13	10	0	3
4	*p*-NO_2	Yes[b]	3.0	86	78	0	8
5	*p*-MeCO	Yes	20	97	80	2	15
6	*p*-Cl	Yes	20	83	78	5	0
7	*p*-MeO	Yes	20	68	68	0	0
8	*p*-NH_2	Yes[b]	20	68	68	0	0
9	*m*-CN	Yes	20	99	81	5	13

[a] Reaction conditions: $T = 100$ °C, N_2 atmosphere, Pd/C 5% catalyst (0.05% mmol Pd), ZC_6H_4X (1.0 mmol), $EtCOOCH{=}CH_2$ (1.5 mmol), Et_3N (1.5 mmol), 10 mL isooctane, 5 ml water, A336 (0.30 mmol). [b] Since the substrate is insoluble in isooctane, toluene was used in its place.

$$p\text{-NO}_2 >> \text{H} \geq m\text{-CN} \geq p\text{-MeCO} \approx p\text{-Cl} \geq p\text{-MeO} \geq p\text{-NH}_2$$

In particular, the fastest coupling was achieved with *p*-nitro-iodobenzene **1d**, which yielded 78% of the Heck product **3d**, after 3 h (entry 4). For comparison, without A336, the reaction of **1d** reached only 13% conversion after 6 hours (entry 3).

Under these conditions, the competitive Ullmann and hydrodehalogenation reactions were relevant for **1g**, which yielded 15% of acetophenone **5g** at near complete conversion (entry 5); and for *m*-iodobenzonitrile **1h** that afforded 5 and 13% of the Ullmann and hydrodeiodination products, respectively (entry 9) at full conversion after 20 h.

In all cases however, A336 is crucial for the Heck reaction. Its presence in catalytic amounts accelerates the reaction by a factor of 10 (compare entries 1, 2 and 3, 4 of Table 2), a promoting effect that was already observed also for the hydrodehalogenation reaction.[29,30]

Iodoarenes with electron withdrawing groups react faster with respect to ones with electron donating ones; in analogy to what has already been observed by other authors, this behaviour is presumably due to the stabilization of the "Ar–Pd–X" species formed by the initial oxidative addition of Ar-X to Pd(0).

The multiphase Heck reaction was conducted with less activated olefins as well—styrene **2b** and acrylonitrile **2c**—in the presence of A336, the results are compiled in Table 3.

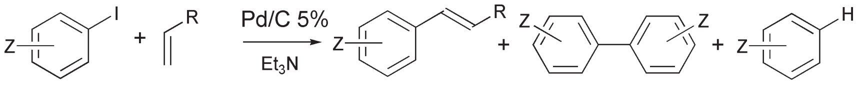
Coupling of **1a** and **2b** produced exclusively stilbene in 46% yield after 20 h (entry 1). Iodoacetophenone **1g** and nitro-iodobenezne **1d** reacted less selectively: after 5.5 h a mixture of products was observed in both cases (entries 2 and 3).

Acrylonitrile **2c** was quite unreactive with **1a**, yielding only traces of cinnamonitrile (entry 4).

The poorer chemoselectivity observed using less activated olefins was particularly pronounced in the presence of an electron withdrawing group on the aryl iodide.

2 Chemoselectivity

A degree of competitive Ullmann coupling—known under similar conditions[31]—was expected. Rather surprisingly however, the major selectivity drawback was due to the formation of the product



3 **4** **5**

(2)

Z = H (**1a**), *p*-MeO (**1c**), *p*-NO_2 (**1d**), *p*-NH_2 (**1e**),
p-Cl (**1f**), *p*-MeCO (**1g**), *m*-CN (**1h**)
R = COOEt (**2a**), Ph (**2b**), CN (**2c**)

Table 3 Multiphase Heck coupling of Z-C_6H_4-I with $CH_2{=}CHR$ [eqn. (2)][a]

Entry	Z	R	A336	Time/h	Conv. (%)	Products (% GC) 3	4	5
1	H	Ph	Y	1.5	10	10	0	0
				20	46	46		
2	*p*-MeCO	Ph	Y	5.5	65	45	5	15
3	*p*-NO_2	Ph	Y[b]	4.5	83	31	43	9
4	H	CN	Y	20	2	<1	1	0

[a] Reaction conditions: $T = 100$ °C, N_2 atmosphere, Pd/C 5% catalyst (0.05% mmol Pd), ZC_6H_4X (1.0 mmol), $RCH{=}CH_2$ (1.5 mmol), Et_3N (1.5 mmol), 10 mL isooctane, 5 ml water, A336 (0.30 mmol). [b] Since the substrate is insoluble in isooctane, toluene was used in its place.

Table 4 Multiphase Heck coupling of Z-C_6H_4-Br with ethyl acrylate[a]

Entry	Z	Solvent	Time/h	Conversion (%)	3 (% by GC)
1	H	A336 (3 mL)	1.5	55	55
			3.5	100	100
2	*p*-MeO	Multiphase	20	1	<1
3	*p*-NO_2	Multiphase*	20	98	96
4	*p*-Cl	Multiphase	20	5	3

[a] Reaction conditions: $T = 100$ °C, N_2 atmosphere, Pd/C 5% catalyst (0.05% mmol Pd), ZC_6H_4Br (1.0 mmol), $EtCO_2CH{=}CH_2$ (1.5 mmol), Et_3N (1.5 mmol), 10 mL *i*-octane, 5 ml water, A336 (0.30 mmol). * Since the substrate is insoluble in isooctane, toluene was used in its place.

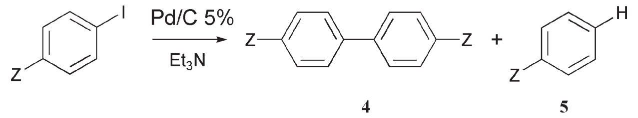
Table 5 Reaction of Ph-I with ethyl acrylate using different bases[a]

Entry	Solvent system	Base	Time/h	Products 4	3
1	A336 solvent[b]	KOH	0.5	5	80
2	A336 + water solvent	KOH	1.0	50	—
3	Solventless	KOH	20	10	10
4	Multiphase	KOH[c]	44	100	—
5	Multiphase	$NaHCO_3$ 4.5%	20	—	50[d]
6	Multiphase	K_2CO_3 10%	20	—	30[d]

[a] Reaction conditions: $T = 100$ °C, N_2 atmosphere, Pd/C 5% catalyst (0.05% mmol Pd), PhI (1.0 mmol), $EtCO_2CH{=}CH_2$ (1.5 mmol), 10 mL isooctane, 5 ml water, A336 (0.30 mmol), KOH (1.5 mmol). [b] 3 ml of Aliquat 336 were used. [c] 5 mL 10% aqueous solution KOH (9 mmol KOH) were used. [d] Reaction becomes inhibited after 30–40% conversion.

deriving from hydrodehalogenation of the substrate (Table 2, entries 4, 5, 9) to give the hydrodehalogenation products, particularly with reactive aryl halides.

To probe the selectivity, the reactions of *p*-nitroiodobenzene **1d** and *p*-iodoacetophenone **1g** were run under the same conditions of entries 4 and 5 of Table 2, but without olefin [eqn. (3)]. After 20 h, **1d** was converted to *p*,*p*′-dinitrobiphenyl **4d** (84%) and nitrobenzene **5d** (16%); while **1g** behaved with opposite chemoselectivity, providing 12% of **4g** and 43% of **5g**.



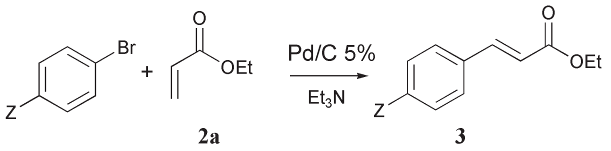
Z = *p*-NO_2 (**1d**), *p*-MeCO (**1g**)

(3)

The relative stability of the Ar-Pd-I species from compound **1d** may have favoured the Ullmann coupling. Instead, the large amount of acetophenone formed from compound **1g**, might be accounted for by a photoinitiated radical mechanism.[32,33] This hypothesis was substantiated by the observation that the reaction of **1g** [eqn. (3)] was suppressed in the absence of triethylamine or water. As well as by the fact that the reaction was inhibited in the presence of air, where oxygen acts as a radical scavenger.

3 Aryl bromides

Iodide produced from the reaction could have been expected to poison the Pd/C catalyst more than bromide and chloride, therefore it was hoped that Ar-Br and Ar-Cl would react more efficiently in the Heck reaction. This however was not the case. The reaction of aryl bromides with ethyl acrylate was carried out under the same conditions of Table 2 [eqn. (4)]. The results are reported in Table 4.



Z = H (**1b**), *p*-MeO (**1j**),
p-NO_2 (**1k**), *p*-Cl (**1l**)

(4)

In the multiphase system, *p*-nitro-bromobenzene **1k** reacted smoothly to yield the Heck product **3d** in 96% yield after 20 h (Table 4, entry 3). Less activated bromides, such as *p*-methoxy- **1j**, and *p*-chloro-bromobenzene **1l**, did not react (entries 2, 4).

4 Effect of the base

Typically, triethylamine is the base of choice for the Heck reaction, but also inorganic bases can be used under aqueous-PTC conditions.[34] A preliminary investigation was undertaken, to determine if under the multiphase conditions the base could be changed to an advantage.

Three inorganic bases were tested in the reaction of Ph-I **1a** with ethyl acrylate **2a**: KOH, $NaHCO_3$, and K_2CO_3. Some results are listed in Table 5.

In A336 as a solvent, with KOH, the Heck product **3a** predominates (80% after 3 h), although 5% of biphenyl **4a** was formed as well. In water as a solvent, with KOH as the base, only **4a** was formed in 50% yield after 1 h. Under solventless conditions (**1a** + **2a** + Pd/C + KOH), an equal mixture of **3a** and **4a** (10% of each) was observed.

Remarkably, when KOH was used as the base under multiphase conditions, the reaction yielded selectively **4a**, in quantitative yield after 44 h. A synergistic effect of base and solvent systems directed selectivity from the exclusive formation of the Heck derived cinnamate (with Et_3N), to the sole formation of biphenyl (KOH).

Carbonate and bicarbonate in the multiphase conditions favoured the selective formation of **3a**, but the reaction became inhibited after approximately 30–40% conversion.

Conclusions

The presence of A336 in conjunction with a supported metal catalyst promotes the Heck reaction, and allows interesting rates to be achieved and selectivity in reactions which involve aryl–halogen bond activation by palladium. In particular, the Heck reaction of aryl iodides with electron poor olefins, becomes up to 10 times faster in the presence of A336 than without, whether it is used as solvent, or in catalytic amounts in the presence of other solvents (organic as well as aqueous).

This enhancement is also observed when A336 is used in catalytic amounts in a multiphase system made by an aqueous–organic mixture. Under these conditions, A336 forms a third liquid phase that allows the catalyst, products and reagents, and base, to be kept separate. This can be regarded as an advantage over solventless systems (where separation and recovery of product and catalyst can be complicated), and over reactions in pure ionic liquids (that are expensive, and that require a product recovery step). In addition, the multiphase system uses a heterogeneous rather than a homogeneous catalyst, and Pd-activating phosphines can be done without.

The nature of the base plays a determining role. While triethylamine steers the system towards the Heck products, KOH favours the production of biphenyl, *via* the Ullmann reaction.

The role played by A336 remains to be fully understood. The rate enhancements may derive from a solvent-effect such as the one observed for the same reaction carried out in the ionic liquid $[bmim]PF_6$ with Pd/C.[18]

What appears important is the interaction of A336 with the supported metal catalyst, as well as its ability to mediate mass transfer between the catalyst and the bulk solution. These effects appear responsible for the changes in rates and selectivity observed in the present case.

Experimental

All reactions were run in a 50 mL round bottomed flask fitted with a reflux condenser, a septum for the withdrawal of samples, and a system for purging with nitrogen. Samples were withdrawn at intervals and analyzed by GC and GC-MS. GC analyses were performed on a Varian 3400 using a fused silica capillary column “Chrompack CP-Sil 24 CB lowbleed/MS” (30 m × 0.25 mm, film thickness 0.25 µm). GC/MS analyses were performed on an Agilent 5973 mass detector coupled to an Agilent 6890N GC with an HP-5MS capillary column (30 m × 0.25 mm, film thickness 0.25 µm). Products were identified by comparison with authentic samples. Reagents, solvents, and catalysts were used as purchased.

Typical multiphase procedure: to the reactor were added, in this order: 1.16 mL 10% wv solution of A336 in isooctane (0.30 mmol A336), 9.0 mL isooctane, 5% Pd/C (106 mg, 0.05 mmol Pd), Et_3N (152 mg, 1.5 mmol), 5.0 mL H_2O, Z-C_6H_4-X (1.0 mmol), $CH_2{=}CH$-R (1.5 mmol). The mixture was heated at the reflux temperature for the desired time.

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