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Catalytic System for the Heck Reaction of Fluorinated Haloaryls

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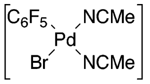
A catalytic system for the Heck reaction of fluorinated haloaryls, which involves the first catalytic insertion into a metal−perfluoroaryl bond, has been developed. Pentafluorophenyl complexes of palladium which lack ligands other than halides are used as catalysts. The absence of other ligands besides solvent, halides, and substrates is required for an efficient functionalization. Pentafluoro- and tetrafluoro-substituted haloaryls can be efficiently reacted with terminal and disubstituted olefins, such as styrene, α-methylstyrene, and acrylate esters, but nonactivated alkenes give only moderate yields. Coordination−insertion is rate determining for pentafluoroaryl and tetrafluoroaryl bromides, which can be switched to oxidative addition if a large excess of olefin is used. Thus, the best reaction conditions can be reached by adjusting the actual ratio of haloaryl to olefin for each combination of substrates.

Introduction

The substitution of an alkyl or aryl group by the corresponding fluorinated analogue modifies, often interestingly, the properties of the parent compounds. This strategy has been used in the synthesis of materials such as polymers and liquid crystals.[1] The functionalization of perfluorinated compounds is also important for the fine chemical and pharmaceutical industries.[2] Thus, the development of catalytic systems capable of introducing fluorinated groups is an important goal.

Arylation of olefins can be easily achieved for regular aryls using the well-known catalytic Heck process.[3] A key step in this palladium-catalyzed process is alkene insertion into the Pd−C bond.[4] However, M−Rf σ-bonds between transition metals and perfluorinated groups are particularly strong and reluctant to reaction. In fact very few stoichiometric and, as far as we know, no *catalytic* reactions based on insertion of unsaturated molecules into M−Rf bonds have been reported. Some of us had studied the insertion of dienes into the Pd−C_6F_5 bond of $[Pd(C_6F_5)Br(NCMe)_2]$ (**1**) and $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2Br_2]$ (**2a**), which led to the observation and isolation of intermediates in the Heck reaction.[5] This experience encouraged us to find a catalytic system for the Heck reaction of perfluoroaryls. Despite the high improvement experienced by the Heck reaction in the past few years, linked to the discovery of very active catalysts, and the use of new reaction conditions,[6−10] no perfluoroaryl or perfluoroalkyl halides have been reported as substrates.[11] We briefly communicated recently the first *catalytic* Heck reaction involving olefin insertion into a C_6F_5−Pd bond, using **1** and **2a** as efficient catalyst precursors.[12] The reaction works in the absence of stabilizing ligands other than halide, the



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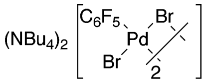

2a

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Table 1. Selected Results for the Heck Reaction in Eq 1 Using 2a as Catalyst Precursor[a]

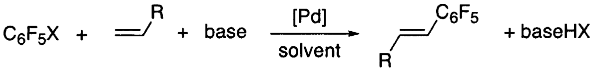
	ArX	olefin	base	amt of Pd (mol %)	time	yield (%)
1	C_6F_5Br	styrene	$CaCO_3$	1	1 day	98
2	C_6F_5Br	styrene	$CaCO_3$	0.1	6 days	97
3	C_6F_5Br	styrene	$CaCO_3$	0.01	15 days	47
4	C_6F_5I	styrene	$CaCO_3$	1	1 day	8
5	C_6F_5Cl	styrene	$CaCO_3$	1	1 day	2
6[b]	C_6F_5Br	Me-acrylate	KF	1	7 h	80
7[b]	C_6F_5Br	Me-acrylate	$CaCO_3$	1	10 h	36

[a] The reactions were carried out with 2.29 mmol of ArX, 2.52 mmol (3.44 mmol for entries 2 and 3) of alkene, 2.52 mmol of base, and H_2O (0.1 mL)[14] in 4 mL of NMP at 130 °C. Yields were determined by ^{19}F NMR in the reaction mixture. [b] At 100 °C.

solvent, and the reagents.[13] Here we give the complete account of the scope and mechanism of this catalytic system, using perfluorinated and partially fluorinated aryls.

Results and Discussion

Catalytic Heck Reactions using C_6F_5X. Complexes **1** and **2a** catalyze the reaction of C_6F_5Br and styrene to give *trans*-PhCH=CHC$_6$F$_5$ regioselectively (eq 1). Methyl acrylate also reacts similarly. Since solutions of **1** in the presence of bromide immediately afford **2a**, after the first catalytic cycle (where bromide is generated as byproduct) catalyst **1** is essentially equivalent to **2a**. For this reason the experiments are usually discussed for **2a**. A summary of results is given in Table 1.



(1)

[Pd] = **1** or **2a** ; R = Ph, CO_2Me

Among the bases examined, $CaCO_3$, KF, and Na_2CO_3 gave the highest yields. Na_3PO_4, ^tBuOK, Na_2CO_3/NEt_3, and Na_2CO_3/collidine slowed the reaction down or led to the formation of C_6F_5H. NaOAc and NaOH gave fast reactions but poor yields, and products of nucleophilic substitution of the para fluorine by acetate or OH were formed. NMP was the best solvent, whereas ^iPrCN, dioxane, and xylene gave poor results.

Almost complete conversion of C_6F_5Br and styrene into pentafluorostilbene was achieved with **2a** at 130 °C (entries 1 and 2, Table 1), even with just 0.1 mol % of catalyst. Lower catalyst loading led to lower yields (entry 3, Table 1). Surprisingly, substantially lower conversion was observed for C_6F_5I (entry 4, Table 1). C_6F_5Cl failed to react with styrene under the same conditions (entry 5, Table 1). An activated alkene, methyl acrylate, reacted more quickly. In this case, the use of KF as base led to higher conversions (entries 6 and 7, Table 1).

Table 2. Selected Results for the Heck Reaction of C_6F_5Br and Several Olefins[a]

	olefin	ArX: olefin	additive (amt (mol %))	Pd (amt (mol %))	yield (%)[b]	C_6F_5H (%)
1	butyl vinyl ether	1:4	NBu_4Br (10)	**2a** (2)	28	27
2	2,3-dihydrofuran	1:5	NBu_4Br (10)	**2a** (4)	10	12
3	2,5-dihydrofuran	1:2		**2a** (1)	18	41
4	1-hexene	1:1.1		**2a** (1)	37	6
5	1-hexene	1:4		**2a** (2)	50	3
6	cyclohexene	1:20		**2a** (2)	14	18
7	methylenecyclohexane	1:5		**2a** (2)	11	
8	α-methylstyrene	1:1.4	NBu_4Br (10)	**1** (2)	79	14

[a] The reactions were carried out with 2.29 mmol of ArX, 2.52 mmol of $CaCO_3$, and H_2O (0.1 mL) in 4 mL of NMP at 130 °C. The reaction time was 1 day, except for entry 8 (5 days); yields were determined by ^{19}F NMR of the reaction mixture. [b] Mixtures of isomers are obtained in most cases.

The influence of the relative ratio of reactants was also tested. The yield of pentafluorostilbene obtained under the conditions of Table 1 but using 2% mol Pd of complex **2a** after 2.5 h was as follows: 36% for the C_6F_5Br to styrene ratio 1:1.1, 43% for the C_6F_5Br to styrene ratio 4:1.1, and 98% for the C_6F_5Br to styrene ratio 1:4.4. Thus, an increase of the relative amount of C_6F_5Br had just a moderate effect on the reaction rate, while it increased markedly in the presence of a 4-fold amount of styrene. However, the use of a large excess of olefin (i.e. C_6F_5Br:styrene = 1:20) was very detrimental and the reaction stopped after very low conversion.

We tested other palladium compounds as catalysts under the conditions given in entry 1 of Table 1. [Pd(PPh$_3$)$_4$] failed to catalyze the reaction of styrene and C_6F_5Br. Palladacycles that are extremely active for other substrates, such as Herrmann's *trans*-bis(μ-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) or the complex $[Pd(C-N)(O_2CCF_3)]_2$ ($C-N = (C_6H_4)C(Me)N^iPr$)[6c] gave only moderate yields (45% and 46%, respectively). Under typical Herrmann conditions (DMA, NaOAc, NBu_4Br, 130 °C),[7b] Herrmann's catalyst was inactive for C_6F_5Br (less than 3% conversion). Other catalysts bearing no additional ligands were tested: $PdCl_2$ is efficiently reduced "in situ" to enter the cycle as Pd(0) and turns out to be as efficient a catalyst as **2a** for the reaction in eq 1, while Pd/C was much less efficient (98% yield was obtained for $PdCl_2$ versus 47% for Pd/C).

Table 2 collects the best conditions found for the reaction of C_6F_5Br with other alkenes. In general 1,1- and 1,2-disubstituted olefins reacted poorly (entries 2, 3, 6, and 7, Table 2), resulting in low to moderate yields of Heck products and formation of significant amounts of the reduction byproduct C_6F_5H. An exception was the activated olefin α-methylstyrene (entry 8, Table 2), which gave a good yield of Heck product. Terminal alkenes such as 1-hexene (entries 4 and 5, Table 2) benefited from the addition of excess olefin. The electron-rich olefin butylvinyl ether (entry 1, Table 2) also reacted poorly. Moreover, it was affected by hydrolysis

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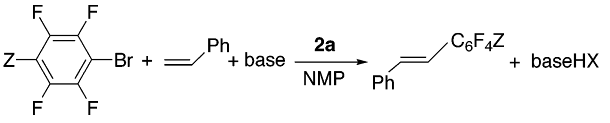
Table 3. Heck Reaction of p-ZC_6F_4Br and Styrene at Partial Conversion Using Precursor 2a[a]

		yield (%)	
	Z	ArBr:olefin = 1:1.1[b]	ArBr:olefin = 1:20[c]
1	OMe	37	9
2	F	36	7
3	CF_3	2	36
4	CN	3	33

[a] Reaction conditions: NMP, **2a** (2 mol % Pd), $CaCO_3$ as base. [b] 130 °C, 2.5 h. [c] 120 °C, 30 min; yields were determined by ^{19}F NMR in the reaction mixture.

processes under the reaction conditions and by Pd-mediated C−O cleavage.[15]

Heck Reactions using Other Fluoroaryls. Styrene reacts with bromotetrafluoroaryls, using catalyst **2a**, to give *trans*-tetrafluoroarylstilbenes (eq 2).



(2)

Z = OMe, CF_3, CN

To evaluate the rate dependence of the arylation reaction on the para substituent of the aryl group, four experiments were carried out, reacting styrene with p-ZC_6F_4Br (Z = OMe, CF_3, CN, F) under the same conditions and quenching the reactions before completion after identical reaction times. The conversions found should reflect roughly the relative reaction rates. The reactivity order found for the molar ratio ArBr:alkene = 1:1.1 was as follows: OMe ≈ F ≫ CF_3 ≈ CN (Table 3). Using the molar ratio ArBr:alkene = 1:20, the reverse order was observed, CN ≈ CF_3 ≫ F ≈ OMe, with the reactions for p-$MeOC_6F_4Br$ and C_6F_5Br stopping at a very early stage. No Hammett correlation was found for the different p-ZC_6F_4Br derivatives (Figure 1).[16] The mechanistic implications of this observation are discussed later.

The Heck reactions of more conventional fluoroaryl halides, such as p-FC_6H_4X (X = Cl, Br, I) and styrene or α-methylstyrene with **2a** (or **1** and added NBu_4Br) as catalyst were also tested. Their behavior showed interesting differences as compared with C_6F_5Br. The results obtained for our system are collected in Table 4.

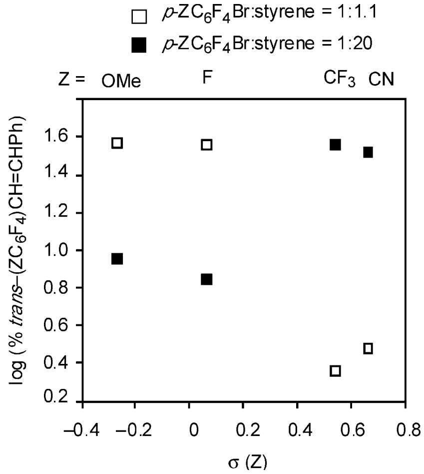


Figure 1. Plot of conversions into trans-$(ZC_6F_4)CH{=}CHPh$ from Table 3 versus Hammet parameters σ for the para substituents (Z) in the ring.

Table 4. Selected Results for the Heck Reaction of p-FC_6H_4X Using 1 as Catalyst Precursor

	ArX	olefin	base	amt of Pd (mol %)	time	yield (%)
1[a]	p-FC_6H_4Br	styrene	Na_2CO_3	1	6 h	100
2[b]	p-FC_6H_4Br	styrene	Na_2CO_3	0.1	1 day	98
3[b]	p-FC_6H_4Br	styrene	Na_2CO_3	0.001	4 days	93
4[a]	p-FC_6H_4Cl	styrene	$CaCO_3$	1	1 day	
5[a]	p-FC_6H_4I	styrene	Na_2CO_3	1	30 h	95
6[a]	p-FC_6H_4Br	α-methylstyrene	$CaCO_3$	2	2 days	55

[a] The reactions were carried out with 2.29 mmol of ArX, 2.52 mmol of alkene, 2.52 mmol of base, NBu_4Br (0.229 mmol), H_2O (0.1 mL) in 8 mL of NMP at 130 °C; yields were determined by ^{19}F NMR in the reaction mixture. [b] Same conditions as (a) scaled 2.5 times (entry 2) or 20-fold (entry 3).

As shown in Table 4, complete conversion and good activity was obtained for p-FC_6H_4Br. The reaction of the iodo derivative was slower, whereas the chloroaryl species was inactive. Similar results were obtained with **2a** as catalyst, without added NBu_4Br. In contrast to the reactions with C_6F_5Br, the reaction rate for p-FC_6H_4Br increased for p-FC_6H_4Br to styrene ratios over 1:1 and decreased when excess olefin was used. The yields of p-$FC_6H_4CH{=}CHPh$ obtained, at 130 °C for 20 min,[17] were as follows: 15% for p-FC_6H_4Br:styrene = 1:4.4; 23% for p-FC_6H_4Br:styrene = 1:1.1; 47% for p-FC_6H_4Br:styrene = 4:1.1. Although more reluctant to reaction, the disubstituted α-methylstyrene underwent substitution in moderate yield (Table 4, entry 6).

Mechanistic Studies. Mechanistic studies were carried out mostly on the reaction of C_6F_5X and styrene catalyzed by **2a**. The mechanism proposed on the basis of these studies is depicted in Scheme 1 and can be used to interpret the pathway followed by other substrates.

Initially a radical pathway was ruled out, since the reaction of C_6F_5Br with styrene was not affected by oxygen or by the addition of galvinoxyl (Pd:galvinoxyl = 1:10), and no products of C_6F_5Br radical addition to the alkene were observed.

In $CDCl_3$ complex **2a** is a 1:1.6 mixture of the two isomers corresponding to the cis and trans arrangements of the two C_6F_5 groups in the dimer. Upon addition of NMP, a new signal appears in the ^{19}F NMR spectrum that increases as the concentration of NMP increases. It is attributed to $[Pd(C_6F_5)Br_2(NMP)]^-$ (**3a**). When **2a** was dissolved in pure NMP, the major species observed at low concentrations and room temperature was **3a**. Upon addition of Br^-, the dianion **4a** was also detected. The equilibrium constants between **2**−**4** in NMP at room temperature were measured by ^{19}F NMR,

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(14) H_2O is added to increase the solubility of salts in the reaction mixture (mainly $CaBr_2$ formed in the reaction course). We did not study in detail the effect of water in the reaction, but we carried out comparative experiments, and a slight increase in conversion was observed with water (36% with 0.1 mL H_2O; 30% without water after 2.5 h reaction time under the conditions of entry 1).

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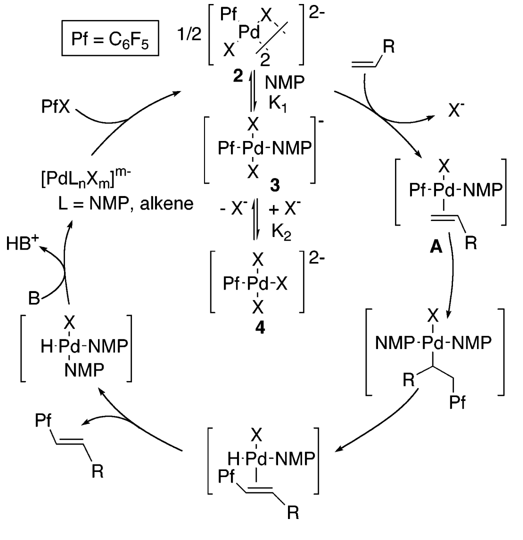
(16) Hammett parameters (Z, σ): OMe, −0.27; F, 0.06; CF_3, 0.54; CN, 0.66 (Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, 91, 165−195). Similar results are obtained using σ^- parameters of Z rather than σ.

(17) NMP as solvent, **2a** (2% mol Pd) as catalyst, and $CaCO_3$ used as base.

Scheme 1. Catalytic Cycle for the Heck Reaction of C_6F_5X and Alkenes



affording the following values: $K_1 = [\mathbf{3}]/[\mathbf{2}]^{1/2} = 0.603 \pm 0.018$, $K_2 = [\mathbf{4}]/[\mathbf{3}][X^-] = 3.20 \pm 0.13$ for X = Br (**a**); $K_1 = 0.180 \pm 0.005$, $K_2 = 3.09 \pm 0.12$ for X = I (**b**). At temperatures close to the catalytic conditions (120 °C) the equilibria in Scheme 1 become fast, and the signals of the three complexes coalesce, preventing measurement of the equilibrium constants.

When the reaction of C_6F_5Br and styrene was monitored by ^{19}F NMR at 120 °C under catalytic conditions, only one set of Pd−C_6F_5 signals (F_{ortho}, −116 ppm), corresponding to the time-averaged fast equilibrium just described, was observed throughout the catalysis. Similar fast equilibria may be affecting other Pd(II) complexes represented in Scheme 1 during the catalytic reaction, but only the solvent-ligated species are represented for brevity.

The first process in the catalytic cycle is the coordination and insertion of the alkene, which is likely to be rate determining. This is supported by the detection throughout the process of the signals of the complexes preceding this step and by two kinetic observations described above: the rate of reaction between C_6F_5Br and styrene catalyzed by **2a** is practically independent of the concentration of aryl bromide, but it increases when the styrene concentration is increased. We could not detect complex **A** (Scheme 1) either under catalytic conditions or in stoichiometric experiments. Thus, the coordination and insertion steps could not be studied separately and we must refer to both processes jointly. Independent reactions out of the catalytic cycle showed that the insertion of styrene into the Pd−C_6F_5 bond of **3a** (synthesized by dissolving **2a** in NMP) was retarded by the addition of NBu_4Br.[18,19] When reactions of isolated **2a** (X = Br) and **2b** (X = I) in NMP with an excess of styrene were monitored, longer reaction times for the iodo derivative **2b** were observed (20% $C_6F_5CH{=}CHPh$ for **2a** versus 3% for **2b**, after 17 h at room temperature). Thus, the slow reaction observed for C_6F_5I in the catalytic cycle may be due to a lower rate of substitution of iodide by the alkene in this step. β-Hydrogen elimination and reductive elimination of HX follow, giving palladium(0) species.

When the catalytic reaction was carried out using bromide-free conditions (adding Ag_2CO_3 as a base to precipitate the bromide formed), only 3% of the coupling product was obtained after 1 day, and extensive catalyst decomposition was observed. Since the olefin insertion in cationic palladium complexes is feasible and fast,[5c] the absence of bromide must be negatively affecting the oxidative addition step. Halide anions are known to stabilize Pd(0) intermediates and also to increase the rate of oxidative addition when coordinated to Pd(0) species.[20] On the other hand, the reaction rate increases with increasing concentration of styrene, because it favors the coordination−insertion process. However, a large excess (C_6F_5Br:styrene = 1:20) stops the reaction. Addition of NBu_4Br to this reaction mixture makes the process effective. These observations suggest that olefin and bromide are competing in the coordination sphere of Pd(0). When the bromide ions on Pd(0) are displaced by the alkene at high concentrations of the latter, the oxidative addition is severely slowed, becoming rate determining, and the cycle is halted.[21] Thus, the success of this catalysis requires finding in each case a compromise between the conditions optimal for the oxidative addition step and those optimal for the coordination−insertion step.

Since coordination−insertion is the rate-limiting step in the absence of a large excess of olefin, functionalization of nonterminal and/or nonactivated olefins with fluoroaryl groups is more difficult, as shown by the results in Table 2. Although some of the reactions benefit from the use of excess olefin, the limit imposed by the overstabilization of Pd(0) species toward oxidative addition prevents good conversions. The amount of C_6F_5H found in each case gives an indication of the sluggishness of the coordination−insertion step, since this undesired side product forms by decomposition of complexes **2** and **3** if they accumulate in the catalytic cycle (Scheme 1).

In the reactions using p-ZC_6F_4Br as substrates monitored by ^{19}F NMR, organometallic species were also observed. They present characteristic F_{ortho} resonances in the region of p-ZC_6F_4Pd species, well separated (ca. 10−20 ppm) from those of p-ZC_6F_4Br or p-ZC_6F_4C species. We attribute these signals to species analogous to **2**−**4**. The results obtained for these substrates can be fitted into the picture discussed above for C_6F_5, taking into account the electron-withdrawing ability of the aryls (as imposed by the Z substituents) and its influence on the two steps that can become rate determining.[16] Thus, when excess alkene is used the reaction proceeds reasonably only with the more electron-withdrawing aryls. Under these conditions the oxidative addition becomes slow and rate determining and, apparently, only these are capable of oxidatively adding

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(18) Percent of $C_6F_5CH{=}HPh$ formed in the reaction of **2a** with styrene (**2a**:styrene = 1:100) in NMP, 60 °C, 1 h: (a) **2a**:Br^- = 1:0, 75%; (b) **2a**:Br^- = 1:1, 69%; (c) **2a**:Br^- = 1:4, 52%.

(19) Under catalytic conditions bromide is formed at each turnover. Provided that the reaction effectively starts, as happens in our case, this soon makes unimportant the NBu_4Br initially added (if any), which has been reported favorable for other catalysis: Jeffery, T. *Tetrahedron* **1996**, *52*, 10113−10130.

(20) (a) Amatore, C.; Jutand, A. *J. Organomet. Chem.* **1999**, *576*, 254−278. (b) Amatore, C.; Jutand, A. *Acc. Chem. Res.* **2000**, *33*, 314−321.

(21) A similar conclusion has been drawn in a theoretical study: Sundermann, A.; Uzan, O.; Martin, J. M. L. *Chem. Eur. J.* **2001**, *7*, 1703−1711.

efficiently to Pd(0). For bromoaryl to alkene ratios close to 1:1 it is the coordination−insertion process that becomes rate determining. The differences among the bromoaryls depend on the relative oxidative addition−insertion rates. For the more electron-withdrawing substituents (CN, CF_3) a slower insertion rate is expected, which leads to low conversions. Moreover, if complexes **3** and **A** (Scheme 1) decompose under the conditions used, the reaction comes to a halt, as observed. For X = F, OMe both the oxidative addition (expected F > OMe) and the insertion (expected OMe > F) are fast enough and the reaction becomes feasible.

Heck reactions with p-FC_6H_4X should follow a similar mechanism, but with qualitative differences. Our results support that the oxidative addition is rate limiting for p-FC_6H_4Br, since an excess of aryl bromide increases the conversion rate, while olefin coordination−insertion is faster than for C_6F_5Br. Thus, under conditions when the oxidative addition is fast the overall conversion is better for p-FC_6H_4Br than for C_6F_5Br. A 4-fold excess of the olefin is enough to reduce seriously the reaction rate of the oxidative addition step with the less active p-FC_6H_4Br, and this factor needs to be carefully controlled.

Faster oxidative addition is expected for p-FC_6H_4I, but the overall reaction rate turns out to be slower (Table 4). This result is analogous to that obtained for C_6F_5I (Table 1). These observations and the stoichiometric reaction described above for **2b** (X = I) and styrene seem to confirm that substitution of an iodo ligand by the olefin is difficult, and this step makes the reaction less efficient, regardless of the faster rate of oxidative addition. Bromoaryls are thus the best compromise in the tradeoff between oxidative addition and coordination−insertion rates.

In conclusion, an efficient catalytic system for the Heck reaction of fluorinated haloaryls has been developed. This catalysis requires conditions exempt of ligands other than halide, solvent, and substrates. The ligandless catalysts can be the easily storable complexes **1** and **2** (useful for mechanistic studies), but also $PdCl_2$, in NMP as solvent and with inexpensive $CaCO_3$ as base. The reaction works for different fluorinated haloaryls on many olefins but looks less promising for electron-rich olefins. The coordination−insertion step is rate determining for pentafluoro- and tetrafluoroaryls. This step can be favored by using excess olefin, but such addition severely slows down the oxidative addition step. Hence, a tradeoff between these opposing effects is needed for an efficient catalysis in each case.

Experimental Section

All manipulations were carried out using Schlenk techniques. ^{1}H and ^{19}F NMR spectra were recorded on Bruker AC-300 and ARX-300 spectrometers. Chemical shifts (in δ units, ppm) were referenced to TMS for ^{1}H and to $CFCl_3$ for ^{19}F. When ^{19}F NMR spectra were recorded in protic solvents, a capillary with a deuterated solvent was used as external reference. The reactants used were commercial products, except p-$OMeC_6F_4Br$, which was prepared from C_6F_4Br and NaOMe in MeOH at 50 °C. The palladium complexes [Pd(C_6F_5)Br(NCMe)$_2$] (**1**),[5a] $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2Br_2(C_6F_5)_2]$ (**2a**),[22] $[Pd(C{-}N)(O_2CCF_3]_2$ (C−N = $(C_6H_4)C(Me)N^iPr$),[6c] and *trans*-bis(μ-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II)[7b] were prepared according to literature methods.

$(NBu_4)_2[Pd_2(\mu\text{-}I)_2I_2(C_6F_5)_2]$ (2b). To a solution of **2a** (0.7000 g, 0.594 mmol) in acetone (20 mL) was added KI (1.1800 g, 7.128 mmol). The mixture was stirred for 2 days, and then it was filtered. The filtrate was evaporated to ca. 5 mL, and water (15 mL) was added. A dark solid precipitated, which was filtered, washed with water, and dried. Yield: 0.800 g, 92%. Anal. Calcd for $C_{44}H_{72}F_{10}I_4Pd_2$: C, 26.34; H, 4.97; N, 1.92. Found: C, 26.49; H, 5.04; N, 2.40.

General Procedure for the Heck Reactions. A 100 mL Schlenk flask was charged with base, the additive (when used), NMP, alkene, ArX, H_2O, and **2a** dissolved in NMP, under an N_2 atmosphere. The amounts used are specified in Tables 1−3. The mixture was stirred and introduced in a preheated oil bath at the reaction temperature. After the time indicated in Tables 1−3, the reaction mixture was checked by ^{19}F NMR and the yields reported in the tables were determined by integration of ^{19}F signals. The mixture was cooled, and addition of water afforded the product as an off-white solid when styrene or α-methylstyrene was used as olefin. The product was recrystallized from *n*-hexane. Fractional distillation was used for other alkenes.

trans-$C_6F_5CH{=}CHPh$[5a] and *trans*-$C_6F_5CH{=}CHCOOMe$[23] have been described before.

trans-*p*-$FC_6H_4CH{=}CHPh$: ^{19}F NMR (282 MHz, δ, $CDCl_3$) −114.68 (m, 1F, F_{para}); ^{1}H NMR (300 MHz, δ, $CDCl_3$) 7.5 (m), 7.36 (m), 7.27 (m), 7.05 (m). Anal. Calcd for $C_{14}H_{11}F$: C, 84.82; H, 5.59; Found: C, 84.33; H, 5.66.

p-$FC_6H_4CH{=}CMePh$: ^{19}F NMR (282 MHz, δ, $CDCl_3$) −116.1 (m, 1F, F_{para}); ^{1}H NMR (300 MHz, δ, $CDCl_3$) 7.5 (m, 2H), 7.3 (m, 5H), 7.08 (m, 2H), 6.81 (m, 1H, CH=), 2.26 (s, 3H, Me). Anal. Calcd for $C_{15}H_{13}F$: C, 84.89; H, 6.17; Found: C, 84.16; H, 6.26.

The products obtained in the reaction of p-ZC_6F_4Br (Z = CN, CF_3, OMe) with styrene or C_6F_5Br and olefins other than styrene were not isolated, and conversions were determined by ^{19}F NMR.

trans-4-$CNC_6F_4CH{=}CHPh$: ^{19}F NMR (282 MHz, δ, NMP, acetone-d_6 capillary) −141.32 (m, 2F) −136.11 (m, 2F).

trans-4-$CF_3C_6F_4CH{=}CHPh$: ^{19}F NMR (282 MHz, δ, NMP, acetone-d_6 capillary) −143.70 (m, 2F), −141.67 (m, 2F), −56.01(s, 3F, CF_3).

trans-4-$OMeC_6F_4CH{=}CHPh$: ^{19}F NMR (282 MHz, δ, NMP, acetone-d_6 capillary) −159.50 (m, 2F), −145.20 (m, 2F).

3-(Pentafluorophenyl)-2,3-dihydrofuran: ^{19}F NMR (282 MHz, δ, NMP, acetone-d_6 capillary) −141.2 (m, 2F, F_{ortho}), −161.2 (t, 1F, F_{para}), −164.8 (m, 2F, F_{meta}).

(Pentafluorophenyl)cyclohexene: ^{19}F NMR (282 MHz, δ, NMP, acetone-d_6 capillary) −143.9 (m, 2F, F_{ortho}), −159.4 (t, 1F, F_{para}), −164.2 (m, 2F, F_{meta}).

$C_6F_5CH{=}CMePh$ (mixture of two isomers): ^{19}F NMR (282 MHz, δ, NMP, acetone-d_6 capillary) −140.4 (m, 2F, F_{ortho}), −157.8 (t, 1F, F_{para}), −164.1 (m, 2F, F_{meta}) and −143.8 (m, 2F, F_{ortho}), −158.3 (t, 1F, F_{para}), −164.1 (m, 2F, F_{meta}).

Determination of Equilibrium Constants. We prepared 0.01 M solutions of **2** in NMP (for determination of K_1), 0.1 M solutions of **2**, and 0.02 M solutions of NBu_4X in NMP (for determination of K_2). The concentration of the species formed was determined by integration of their ^{19}F NMR signals at room temperature. ^{19}F NMR (δ, NMP (acetone-d_6 capillary; F_{meta}, F_{para}, F_{ortho}; 282 MHz): **2a**, −166.61 (cis + trans), −164.50, −164.35 (cis + trans), −116.79 (cis + trans). **3a**, −168.18, −166.35, −116.02; **4a**, −168.62 (F_{para} + F_{meta}), −114.91; **2b**, −166.53 (cis + trans), −164.88, 164.66 (cis + trans), −112.35 (cis + trans); **3b**, −168.61, −166.71, −112.59; **4b**, −168.75 (F_{para} + F_{meta}), −111.67.

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