



Non-Chelate-Assisted Palladium-Catalyzed Aerobic Oxidative Heck Reaction of Fluorobenzenes and Other Arenes: When Does the C–H Activation Need Help?

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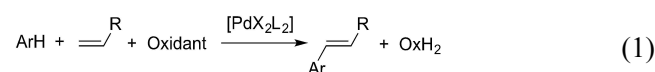
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Abstract: The pyridone fragment in the ligand [2, 2'-bipyridin]-6(1*H*)-one (bipy-6-OH) enables the oxidative Heck reaction of simple arenes with oxygen as the sole oxidant and no redox mediator. Arenes with either electron-donating or electron-withdrawing groups can be functionalized in this way. Experimental data on the reaction with toluene as the model arene shows that the C–H activation step is turnover limiting and that the ligand structure is crucial to facilitate the reaction, which supports the involvement of the pyridone fragment in the C–H activation step. In the case of fluoroarenes, the alkenylation of mono and 1,2-difluoro benzenes requires the presence of bipy-6-OH. In contrast, this ligand is detrimental for the alkenylation of 1,3-difluoro, tri, tetra and pentafluoro benzenes which can be carried out using just [Pd(OAc)₂]. This correlates with the acidity of the fluoroarenes, the most acidic undergoing easier C–H activation so other steps of the reaction such as the coordination-insertion of the olefin become kinetically important for polyfluorinated arenes. The use of just a catalytic amount of sodium molybdate as a base proved to be optimal in all these reactions.

Keywords: C–H activation; olefination; palladium; ligand cooperation; oxygen; arenes

Introduction

The Fujiwara-Moritani or oxidative Heck reaction of arenes has gained great importance in the cross-coupling toolbox of the synthetic chemist (Eq. 1).



Mostly catalyzed by palladium complexes, it has been applied in an intra- and intermolecular fashion for the alkenylation of arenes, often bearing directing groups (chelate-assisted functionalization), and these advances have been collected in several reviews.^[1–7] The use of arenes as reactants instead of the aryl halides in the conventional Heck reaction is a clear advantage as far as sustainability is concerned. However, the reaction needs a stoichiometric amount of an

oxidant and, depending on its identity, this may erode the atom economy of the reaction and introduce toxicity issues. This is the case of the common copper derivatives, silver salts, benzoquinone or peroxides.^[8] Aerobic oxidative Heck reactions lack these problems and oxygen as the sole oxidant is the cleanest and most attractive choice. A compromise approach that uses oxygen and a catalytic amount of the above-mentioned oxidants or other redox mediators such as ferrocenium salts or iron phthalocyanine derivatives has also been applied.^[9]

Oxygen as oxidant has been used in chelate-assisted oxidative Heck reactions, and also in the alkenylation of arenes with no directing groups (simple arenes). The latter are more difficult to activate since they lack a coordinating group that facilitates the approach of the arene group to the metal in a chelating fashion and the subsequent C–H activation. However, a variety of

conditions have been developed for fluoroarenes,^[10,11] heterocycles,^[12–17] and other simple arenes,^[9,18–25] which are often very specific for the particular reactant combination.

In order to further improve these processes and within the framework of the accepted mechanism for this reaction (Scheme 1), the attention is generally focused in the two steps which are considered crucial to reach an efficient catalytic aerobic arene alkenylation reaction: The usually energy demanding C–H activation step, and the palladium(0) oxidation step which can compete with metal aggregation and catalyst deactivation. The Pd(0) oxidation by oxygen has been studied, and this step is not usually rate limiting although other factors such as the intrinsic solubility of the gas and mass-transfer problems can play a role in the efficiency of the oxidation and the catalyst performance.^[26]

As can be gathered from the catalytic cycle in Scheme 1, the C–H activation step can benefit from the presence of a base (also the palladium hydride decomposition to Pd(0)), but the oxidation step needs the protonation of the putative peroxy palladium complex formed by reaction with oxygen. Therefore, the choice of additives in these reactions is not always straightforward and a delicate balance is required.

The C–H activation step can be favored by the use of cooperating ligands that act as an intramolecular base in the transition state of C–H activation by a concerted metalation-deprotonation (CMD) mechanism. In the context of the oxidative Heck reaction of arenes, acyl mono-protected amino acids (MPAA), a potential cooperating type of ligands, have been used,^[27] sometimes in combination with a second ligand,^[28–30] and they have shown a positive effect in the aerobic olefination of arenes bearing directing groups.^[31–33] Pyridone-type ligands can also assist the

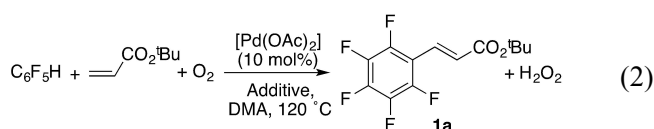
C–H cleavage step, and there are a few examples of their use in olefination processes with silver oxidants,^[34–36] and with stoichiometric Cu(II) salts or a O₂/Cu(II) salt mixture.^[19,37] Upon lowering the activation energy of the C–H cleavage step in the presence of a cooperating ligand, other steps in the catalytic cycle can become turnover limiting and this has been shown recently in the change in regioselectivity observed in the Cu(II)/O₂ mediated alkenylation of indole derivatives.^[37]

We report here the efficient oxidative Heck reaction with oxygen at atmospheric pressure as the sole oxidant of a number of fluoroarenes and other arenes with different substituents using the cooperating ligand [2, 2'-bipyridin]-6(1*H*)-one (bipy-6-OH). We have previously employed this ligand for the direct arylation of arenes and shown its role in assisting the C–H activation step.^[38,39] Now, a set of reaction conditions have been developed for the oxidative Heck reaction that use minimum amount of additives (acids or bases) and can be applied to a variety of simple arenes. The nature of the arene influences the step that controls the alkenylation reaction and we have studied when the cooperation of the ligand is crucial and those cases where the C–H cleavage is fast enough, so the assistance of the ligand in the C–H activation is not required.

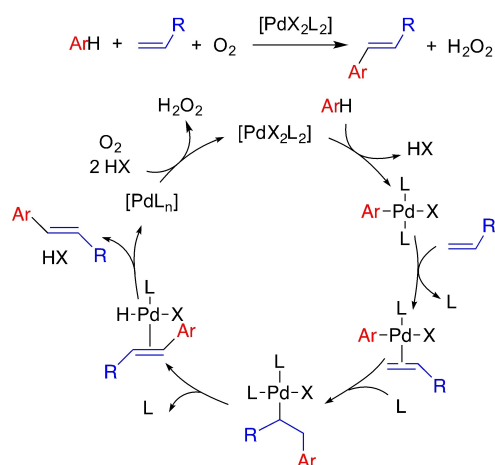
Results and Discussion

Oxidative Heck Reactions of Fluorinated and Non-Fluorinated Arenes

The reaction of pentafluorobenzene with *t*-butyl acrylate was first tested and used to set up suitable reaction conditions (Eq. 2).



The reaction was carried out using a moderate excess of the arene (2.5 equivalents) in DMA as solvent. Acids and/or bases, sometimes in excess, are commonly used as additives in these reactions, and which one to choose is often difficult to anticipate. They are not reactants in the aerobic Heck reaction, as shown in Scheme 1 and Eq. 2, although several proton transfer processes occur in the reaction that can be favored by these additives. We found that just a catalytic amount of base (10 mol%) is needed to ensure good yields, whereas an excess of base or an acid is detrimental (Table 1, entries 1–6). This has also been observed in other aerobic Pd-catalyzed oxidative couplings.^[40] Sodium molybdate (pK_a (HMoO₄[−]) = 3.5–4.5)^[41,42] gives excellent results and works better



Scheme 1. Palladium-catalyzed oxidative Heck reaction of arenes and general mechanism.

Table 1. Oxidative Heck reaction of C_6F_5H according to Eq. 2.^[a]

Entry	[Pd]	Additive (equiv.)	1a , crude yield, %, 6 h ^[b]
1	[Pd(OAc) ₂]	–	0
2	[Pd(OAc) ₂]	AcOH (1.5)	15
3	[Pd(OAc) ₂]	CS ₂ CO ₃ (1.5)	0
4	[Pd(OAc) ₂]	CS ₂ CO ₃ (0.1)	76
5	[Pd(OAc) ₂]	NaOAc (0.1)	61
6	[Pd(OAc) ₂]	Na ₂ MoO ₄ ·2H ₂ O (0.1)	99 (88 ^{isol})
7	–	Na ₂ MoO ₄ ·2H ₂ O (0.1)	0
8 ^[c]	[Pd(OAc) ₂]	Na ₂ MoO ₄ ·2H ₂ O (0.1)	67
9 ^[d]	[Pd(OAc) ₂]	Na ₂ MoO ₄ ·2H ₂ O (0.1)	5
10 ^[d]	[Pd(OAc) ₂]	Na ₂ MoO ₄ ·2H ₂ O (1)	0
11 ^[d]	[Pd(OAc) ₂]	Na ₂ MoO ₄ ·2H ₂ O (0.1) + H ₂ O ₂ (1)	7
12 ^[e]	[Pd(OAc) ₂]	Na ₂ MoO ₄ ·2H ₂ O (0.1)	81
13 ^[f]	[Pd(OAc) ₂]	Na ₂ MoO ₄ ·2H ₂ O (0.1)	27 ^{g)}
14	[Pd(OAc) ₂] ^{h)}	Na ₂ MoO ₄ ·2H ₂ O (0.1)	86
15	[PdCl ₂ (NCMe) ₂]	Na ₂ MoO ₄ ·2H ₂ O (0.1)	30
16	[PdCl ₂ (NCMe) ₂]	Na ₂ MoO ₄ ·2H ₂ O (0.3)	51
17	[PdCl ₂ (NCMe) ₂]	Na ₂ MoO ₄ ·2H ₂ O (0.1) + NaOAc 3H ₂ O (0.2)	68
18 ⁱ⁾	[Pd(OAc) ₂] ^{g)}	Na ₂ MoO ₄ ·2H ₂ O (0.1)	68 (62 ^{isol})

^[a] Reaction conditions: [Pd(OAc)₂] (0.034 mmol, 10 mol%), C_6F_5H (0.853 mmol), *t*-butylacrylate (0.341 mmol), DMA (3 mL), 120 °C, O₂ (1 atm), unless otherwise noted.

^[b] Crude yields were determined by ¹H NMR using dodecane as internal standard.

^[c] Air instead of O₂.

^[d] Under N₂.

^[e] 90 °C.

^[f] 60 °C.

^[g] 88% yield in 48 h.

^[h] 5 mol%.

^{[i)} Styrene as olefin and $C_6F_5CH=CHPh$ (**1b**) as product.

than other bases (Table 1, entries 4–6). We have no evidence that Na₂MoO₄ is playing a role as redox mediator in the reaction and it may just be acting as a weak base. We run several tests that support that the presence of such a high-valent metal species is not influencing the oxidation process. Mo(VI) is not acting as a terminal oxidant (Table 1, entry 10) and oxygen is necessary (cf. entries 6, 8 (air) and 9 (under N₂), Table 1). The photochemical generation of a more reactive singlet oxygen in the presence of molybdate is not probable since the reaction also works in the dark and a thioether oxidation to a sulfoxide by oxygen transfer, a typical singlet oxygen test, does not work in the reaction conditions used here (see SI). The generation of singlet oxygen by decomposition of hydrogen peroxide in the presence of molybdate has been reported,^[43] and this could occur in the reaction course upon generation of H₂O₂ (Eq. 2).^[44] However, H₂O₂ in the presence of molybdate is not a suitable

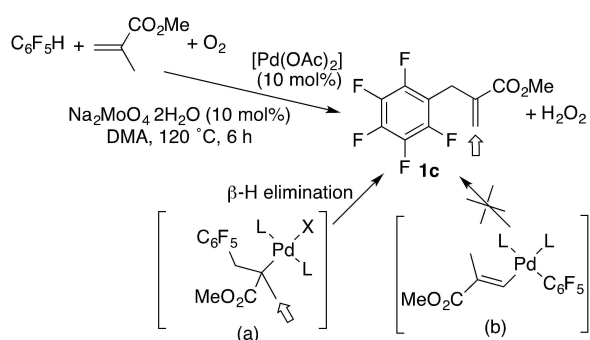
oxidant in this reaction (Table 1, entry 11). We found that sodium tungstate is as efficient as sodium molybdate but other dioxomolybdenum complexes that are active in oxygen-transfer reactions do not work (see SI). Sodium molybdate dihydrate has not been used in this type of reactions and it may seem an unconventional choice, but it is a non-hygroscopic, inexpensive and available salt, which can be used in a very convenient way. It has to be noted that heteropolymolybdates containing redox active vanadium(V) centers have been used as redox mediators in Pd-catalyzed oxidative C–H activation reactions,^[45,46] and greatly developed by Ishii, Obora and co-workers.^[23,47–49] They found that the presence of V(V) is necessary for the redox mediation, as tested in the oxidation of hydroquinone to benzoquinone with oxygen.^[50] We performed the same reaction using Na₂MoO₄ and found that the oxidation is inefficient (see SI).

The reaction can be carried out in milder conditions and the temperature can be lowered to 90 °C or even 60 °C, provided the reaction times are extended to 48 h for the latter (entries 12 and 13, Table 1). The amount of catalyst can be reduced to 5 mol% (Table 1, entry 14). [Pd(OAc)₂] is the best catalyst precursor (cf. entries 6 and 15, Table 1) and for less basic ligands in the precatalyst coordination sphere (Cl vs OAc) the reaction benefits from the presence of additional base and acetate (Table 1, entries 15–17). Other precursor complexes such as [Pd(acac)₂] or [Pd(TFA)₂] in the same conditions as entry 15 were even less efficient (see SI).

Pentafluorostilbene can be prepared by arylation of styrene using this reaction (entry 18, table 1), but the fluoroarylation of olefins with no electron withdrawing groups such as 1-hexene or 2,3-dihydrofuran could not be achieved.

The formation of **1a** (Eq. 2) could be either the result of an oxidative Heck reaction (Scheme 1) or the product of a double C(sp²)-H activation (arene and alkene) and reductive elimination. The reaction of pentafluorobenzene with methyl methacrylate rules out the second route, since the product of this reaction, the terminal olefin **1c**, can only be formed by insertion of the olefin into the Pd–C₆F₅ bond and subsequent β-H elimination, much more favorable for the methyl hydrogens (Scheme 2).

The reaction course was monitored at 80 °C by NMR and the rate of the reaction showed no dependence on the concentration of olefin, arene and catalyst. This points to O₂, whose solubility is quite low in DMA (5.2 mM),^[51] as the factor controlling the reaction rate by keeping the amount of available oxidant as the limiting reagent. This has been observed before for other aerobic reactions in solvents of low oxygen solubility such as DMSO.^[52] An increase of the



Scheme 2. Perfluoroarylation of methyl methacrylate: it rules out the double C–H activation pathway (intermediate b) vs a Heck route (intermediate a).

O₂ pressure leads to a higher yield (68% yield at 2 atm vs 52% at 1 atm after 20 min).

These results show that the aerobic alkenylation of pentafluorophenyl is efficient without the addition of a cooperating ligand. Indeed, the C–H cleavage of C₆F₅H is facile as can be seen in the monitorization of the reaction in Eq. 2 using C₆F₅D as reagent at 80 °C.

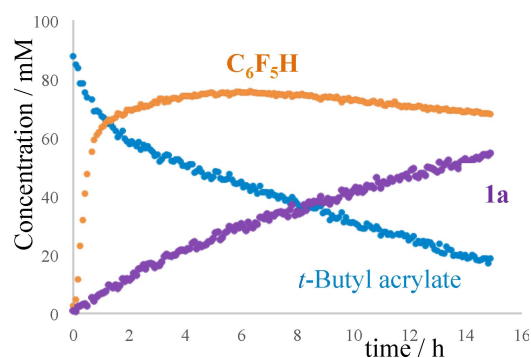
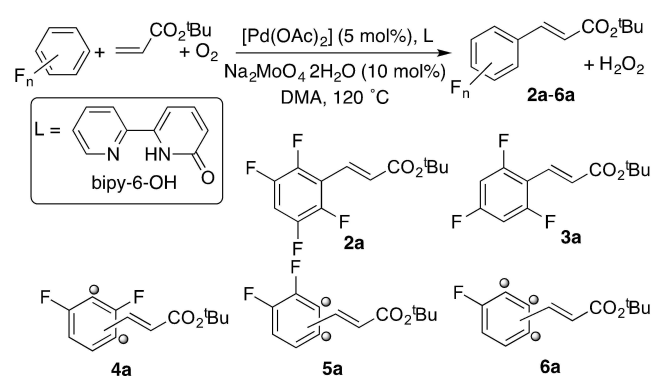


Figure 1. Evolution of the reaction of C₆F₅D and *t*-Bu-acrylate (Eq.2) at 80 °C showing the fast H/D exchange of the arene.



Scheme 3. Aerobic oxidative Heck reaction of fluorinated arenes (○ alkenylated positions).

In the first hour almost all the deuterated arene is converted into C₆F₅H. (Figure 1).^[53]

This conversion is easy in the presence of base and does not require metal catalysis as has been reported before.^[54] In this case just the presence of a catalytic amount of sodium molybdate in the presence of traces of H₂O is enough for the conversion, as we tested independently (see SI). Nonetheless, the presence of acetate in the reaction plays a beneficial role which points to the occurrence of an acetate-mediated CMD route to generate the Pd–C₆F₅ bond (Table 1, entry 17).

The alkenylation of other fluorinated arenes can also be carried out and the best reaction conditions found show the increasing importance of the C–H cleavage in the reaction upon decreasing the number of fluorine substituents (Scheme 3 and Table 2).

Tetrafluorobenzene can be alkenylated in moderate yield using a 2.5-fold excess of the arene in the same way used for pentafluorobenzene. In both cases the use of a higher amount of the arene has no influence in the reaction outcome (entries 1 and 2, Table 2, and Table S1). In contrast, the reactions with trifluorobenzene and 1,3-difluorobenzene clearly benefit from the use of a larger excess of arene (5-fold, cf. entries 3, 4 and 5, 6, Table 2). This indicates that the arene

Table 2. Oxidative Heck reaction of C₆F_nH_{6-n} according to Scheme 3.^[a]

Entry	Arene (equiv.)	L mol %	Crude yield (%) 6 h ^[b]	Crude yield (isol.) (%) 24 h ^[b]
1	1,2,4,5-C ₆ F ₄ H ₂ (2.5)	–	2 a, 48	
2	1,2,4,5-C ₆ F ₄ H ₂ (5)	–	2 a, 50	2 a, 56 (42)
3	1,3,5-C ₆ F ₃ H ₃ (2.5)	–	3 a, 52	
4	1,3,5-C ₆ F ₃ H ₃ (5)	–	3 a, 71	3 a, 71 (60)
5	1,3-C ₆ F ₂ H ₄ (2.5)	–	3 a, 46	
6	1,3-C ₆ F ₂ H ₄ (5)	–	4 a, 68	4 a, 99 ^[c] (85)
7 ^[d]	1,3-C ₆ F ₂ H ₄ (2.5)	–	4 a, 44	
8	1,2-C ₆ F ₂ H ₄ (2.5)	–	5 a, 13	
9 ^[e]	1,2-C ₆ F ₂ H ₄ (44)	–	5 a, 20	
10 ^[e]	1,2-C ₆ F ₂ H ₄ (44)	5	5 a, 60	5 a, 86 ^[f] (75)
11 ^[e]	C ₆ FH ₅ (47)	–	6 a, 18	
12 ^[e]	C ₆ FH ₅ (47)	5	6 a, 75	6 a, 87 ^[g] (78)

^[a] Reaction conditions: [Pd(OAc)₂] (0.017 mmol, 5 mol%), *t*-butylacrylate (0.341 mmol), Na₂MoO₄·2H₂O (0.034 mmol, 10 mol%), DMA as solvent (3 mL), 120 °C, O₂ (1 atm), unless otherwise noted.

^[b] Crude yields were determined by ¹H NMR using dodecane as internal standard.

^[c] Isomer ratio 2,6-F₂:2,4-F₂ = 2:1.

^[d] *t*-Butylacrylate (2 equiv.).

^[e] Arene:DMA = 1:1 v/v.

^[f] Isomer ratio 2,3-F₂:3,4-F₂ = 1.8/1.

^[g] Isomer ratio o:m:p = 2.8:3.8:1.

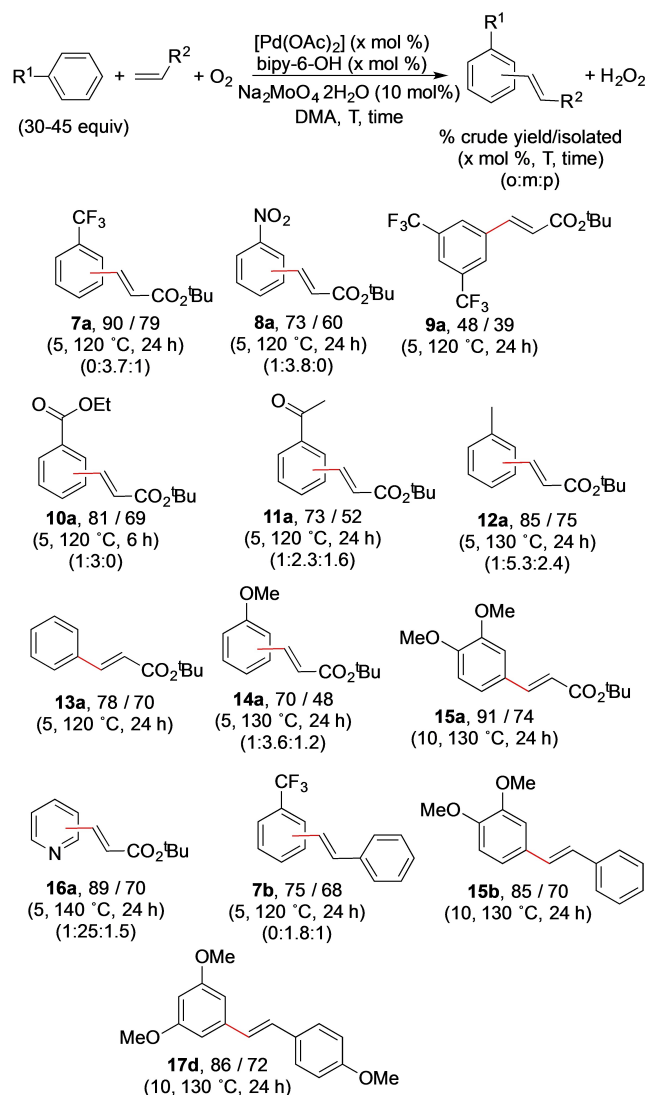
activation is kinetically relevant for these arenes but the excess of olefin has no effect (Table 2, entries 5–7). The alkenylation of 1,2-difluorobenzene or fluorobenzene is inefficient even when using a large excess of arene, and it reaches good yields only in the presence of the ligand bipy-6-OH. The observed reactivity for the fluoroarenes fits the acidity trend of the C–H bond that is cleaved,^[54] which in turn parallels the ease of C–H activation also favored by the stronger Pd–C bond for fluoroaryls with ortho fluorines.^[55] As the F-substitution decreases the C–H activation becomes turnover limiting and eventually needs the assistance of bipy-6-OH. It has to be noted that, in fact, the presence of bipy-6-OH is detrimental for the most reactive penta- tetra- tri- and 1,3-difluorobenzenes, as will be discussed below.

Other non-fluorinated simple arenes were alkenylated using the bipy-6-OH ligand and a catalytic amount of sodium molybdate, in the same way as the less substituted fluoroarenes. Scheme 4 shows the products obtained and the best reaction conditions ([Pd] mol % and T) in each case.

The reaction is useful for arenes bearing electron-withdrawing and electron-donating groups. The alkene stereochemistry in all the products is *trans*, but the C–H activation is not regioselective for the mono-substituted arenes and mixtures of two or three of the ortho, meta and para isomers were found. The meta isomer is always the major one, especially in the case of pyridine. This regiochemistry in the C–H activation is the same observed in the non-oxidative direct arylation reactions with the same ligand.^[38,39] The presence of an ester (**10 a**) or keto (**11 a**) substituent in the arene does not provide a directing effect in this reaction that could shift the regioselectivity towards the ortho isomer. On the other hand, the disubstituted arenes lead to just one isomer regioselectively. In the case of the dimethoxy substituted arenes, this has been used for the synthesis of the resveratrol precursor **17 d** with success.

Mechanistic Aspects and the Role of Bipy-6-OH

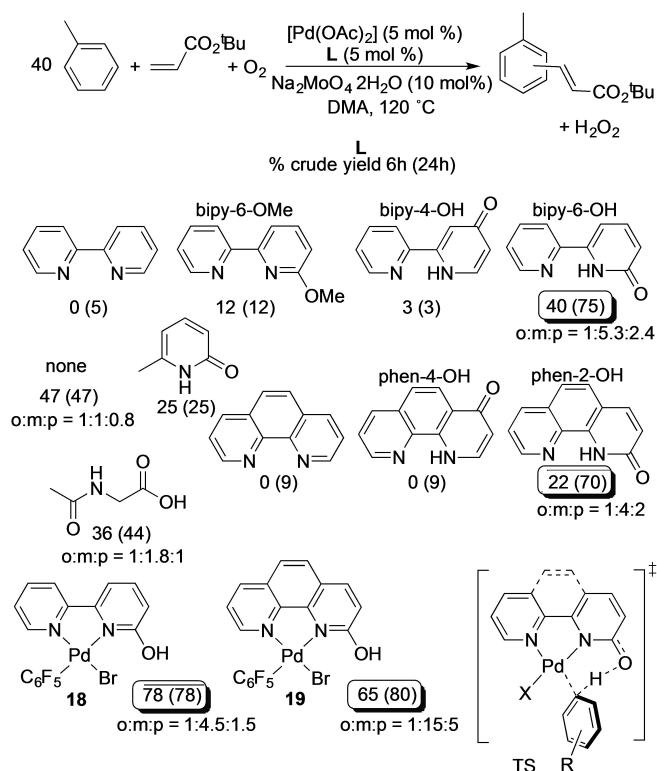
The role of a ligand in a complex catalytic cycle such as that operating in the aerobic oxidative Heck reaction of arenes can be manifold. However, the experimental data point to a cooperating role of bipy-6-OH in the C–H cleavage step in these reactions. Using toluene as a model arene, the kinetic isotope effect was determined using the conditions shown in Scheme 5 (L = bipy-6-OH) for separate reactions using toluene in one experiment and toluene-d₈ in the other. A value of KIE = 2.2 ± 0.2 was obtained, showing that the C–H cleavage is turnover limiting. This value is lower than the one expected for a situation where the C–H activation is the only rate limiting step (KIE ≈ 3.6), indicating that a preceding step, either the coordination



Scheme 4. Aerobic oxidative Heck reaction of non-fluorinated arenes (isomer ratio in the crude mixture).

of the arene or the actual reoxidation rate with O₂, may also be influencing the overall reaction rate, with the C–H cleavage TS being nonetheless the highest in energy and therefore the most influential. This has been discussed before.^[39]

Several catalytic reactions were carried out with different ligands. As can be seen in Scheme 5, only bipy-6-OH and the analogous phen-2-OH have a beneficial effect in the reaction which, along with the KIE found, support the involvement of these ligands in the C–H cleavage via the transition state shown in Scheme 5. Neither the unsubstituted ligands in both N-chelating series (bipy or phen) nor bipy-6-OMe are effective. The position of the pyridone moiety is also crucial, and neither bipy-4-OH nor phen-4-OH enable the reaction. Even if the latter ligands can lead to an



Scheme 5. Aerobic oxidative Heck reaction of toluene with different ligands.

anionic ligand by deprotonation, the pyridone moiety cannot engage in the C–H cleavage.

Phen-2-OH has been used before by Duan et al. in the oxidative Heck reaction of arenes using Cu(II) salts as oxidants or redox mediators.^[19] The authors attributed the observed effect to the anionic (X-L) nature the ligand upon deprotonation which, when compared to a neutral L-L chelating ligand, could facilitate the decooordination of an acetate and the opening of a coordination site on the metal. Although this is certainly plausible, the differences observed between the regioisomers phen-2-OH and phen-4-OH strongly support the direct involvement of the former in the C–H cleavage.

The use of a preformed palladium complex [PdBr(C₆F₅)(L-L)] (L-L = bipy-6-OH, **18**; phen-2-OH, **19**) as precatalyst instead of the mixture [Pd(OAc)₂] + ligand is also effective (Scheme 5). This shows that the presence of acetate is not needed in these reactions, although the moderate yield obtained in the absence of ligand (L = none, Scheme 5) indicates that the C–H cleavage could also occur via a CMD process with an acetato ligand.^[56] In fact, when the mixture [Pd(OAc)₂] + bipy-6-OH is used as precatalyst a putative intermediate complex with both coordinated acetato and bipy-6-O ligands could be involved in the C–H activation step. Which one reacts preferentially is

impossible to ascertain experimentally but DFT calculations on the isolated C–H cleavage step show that the assistance of the bipy-6-OH ligand leads to a lower energy transition state, so the cooperation of this ligand is expected (Figure 2).

Interestingly, a higher selectivity in the alkenylation of toluene towards the meta substitution is observed when bipy-6-OH or phen-2-OH are used (o:m:p = 1:5.3:2.4) than when no ligand is added (o:m:p = 1:1:0.8). This may reflect the different steric requirements in the C–H activation TS for different coordination environments. Recently, the work of Jiao et al. showed that in the alkenylation of indoles using a pyridone derivative as ligand, the regioselectivity is determined by the olefin insertion step.^[37] In our case, the lack of deuteration of **12a** when the reaction was carried out in the presence of D₂O supports an irreversible C–H activation. Also, in contrast to Jiao's work, the reaction is not accelerated when an excess of acrylate is used (see SI). Although deeper studies are needed, these results support that regioselectivity might be determined upon C–H cleavage.

Table 3 shows the effect of bipy-6-OH in the aerobic oxidative Heck reaction of different arenes. An increase of the final yield of the product is observed upon addition of bipy-6-OH in all cases except for the most acidic polyfluoroarenes, where the effect of the ligand is clearly detrimental (Table 3, entries 1–4). Since the C–H activation in these arenes is more facile, the ligand must be hampering other steps in the catalytic cycle, i.e. the coordination-insertion of the olefin.^[57] To test this, we monitored the reaction of *t*-

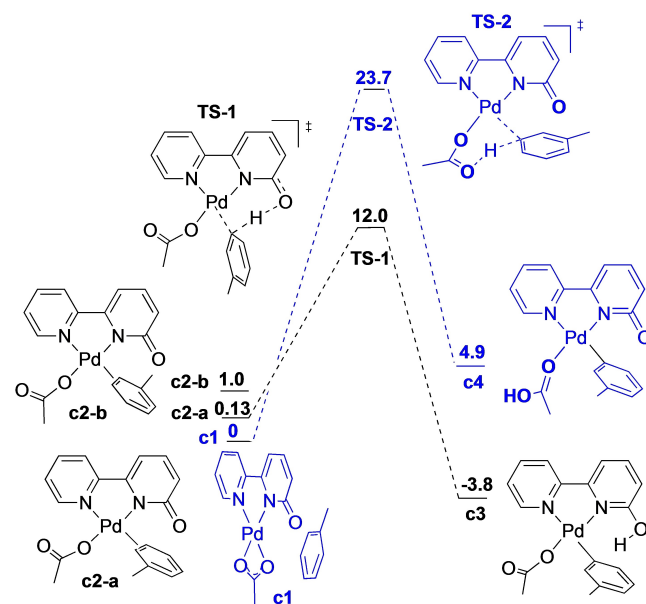


Figure 2. Free energy barriers for the C–H activation step assisted by bipy-6-O or by the acetato ligand. Energies in kcal mol⁻¹.

Table 3. Effect of the use of the ligand bipy-6-OH for the aerobic alkenylation of different arenes with *t*-Bu-acrylate.^[a]

Entry	L	Arene	Cpd.	Crude yield, %	
				6 h ^[b]	24 h ^[b]
1 ^[c]	bipy-6-OH	C ₆ F ₅ H	1a	0	0
2 ^[c]	–	C ₆ F ₅ H	1a	86	90
3 ^[c]	bipy-6-OH	1,3-C ₆ F ₂ H ₄	3a	13	18
4 ^[c]	–	1,3-C ₆ F ₂ H ₄	3a	46	46
5	bipy-6-OH	1,2-C ₆ F ₂ H ₄	5a	60	86
6	–	1,2-C ₆ F ₂ H ₄	5a	20	28
7	bipy-6-OH	PhF	6a	75	87
8	–	PhF	6a	18	18
9	bipy-6-OH	PhCF ₃	7a	72	90
10	–	Ph–CF ₃	7a	40	40
11	bipy-6-OH	PhMe	12a	40	75
12	–	PhMe	12a	47	47
13 ^[d]	bipy-6-OH	1,2-(OMe) ₂ –C ₆ H ₄	15a	73	91
14 ^[d]	–	1,2-(OMe) ₂ –C ₆ H ₄	15a	26	32
15 ^[d,e]	bipy-6-OH	1,3-(OMe) ₂ –C ₆ H ₄	17d	56	86
16 ^[d,e]	–	1,3-(OMe) ₂ –C ₆ H ₄	17d	0	0

^[a] Reaction conditions: [Pd(OAc)₂] (0.017 mmol, 5 mol%), Na₂MoO₄·2H₂O (0.034 mmol, 10 mol%), alkene (0.341 mmol), Arene:DMA=1:1 v/v (total volume, 3 mL), O₂ (1 atm), 120 °C, unless otherwise noted.

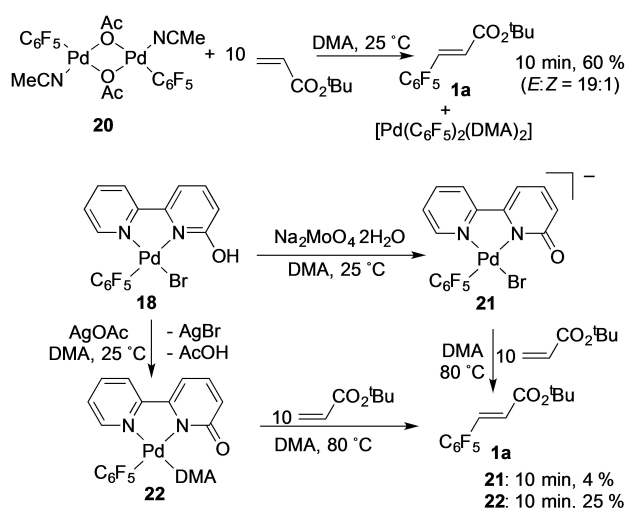
^[b] Crude yields were determined by ¹H NMR using dodecane as internal standard. Yields refer to the mixture of isomers, whose distribution can be found in the SI (Table S3).

^[c] 2.5 equivalents of the arene.

^[d] [Pd(OAc)₂] (10 mol%), L (10 mol%), 130 °C.

^[e] 4-methoxy styrene instead of *t*-Bu acrylate.

butyl acrylate with two palladium complexes that mimic plausible reaction intermediates in both scenarios (Scheme 6).



Scheme 6. Stoichiometric reactions of model palladium complexes with *t*-Bu-acrylate.

The dimeric complex **20** represents the species that could form after C–H activation of C₆F₅H when only [Pd(OAc)₂] is used as precatalyst.

The reaction of **20** in DMA with the olefin is fast and about 60% of the perfluorophenyl acrylate is observed after 10 min at room temperature. A small amount of the *cis* olefination product was also observed as well as the aryl reorganization of the complex to give [Pd(C₆F₅)₂(DMA)₂]. In contrast, complexes **21** and **22** bearing the bipy-6-O ligand only react with *t*-butyl acrylate slowly at 80 °C (Scheme 6). Thus, when the C–H activation is not problematic, the presence of a good chelating ligand, which renders a less accessible metal center, disfavors the coordination of the olefin and the reaction is less efficient. The strong Pd-aryl bond for polyfluoroarenes with ortho substituents also disfavors the insertion of the olefin. The conventional Heck reaction of polyfluoroarenes shows a related situation with the coordination-insertion of the olefin as turnover limiting vs. the most commonly slow oxidative addition.^[58,59]

For some of the arenes in Table 3, the acceleration upon addition of the ligand after 6 h is not very important but, whereas the catalysis does not proceed further without the ligand, it reaches almost completion when bipy-6-OH is added. These results are consistent with the ligand being involved in the stabilization of intermediate species in the cycle. Therefore, the ligand is instrumental to lower the C–H activation energy but its role in the reaction can be more complex affecting other reaction steps, which overall renders a useful olefination reaction.

Conclusion

The oxidative Heck reaction of arenes with oxygen as terminal oxidant and no redox mediators can be carried out using a set of reaction conditions that employ a minimum amount of additives, just sodium molybdate in catalytic amounts, and avoids strongly acidic or basic conditions. The presence of the cooperating [2, 2'-bipyridin]-6(1*H*)-one (bipy-6-OH) ligand enables the reaction for mono and disubstituted arenes of different electronic properties by assisting the C–H activation step. The ligand is detrimental in the olefination of polyfluorinated arenes C₆F_nH_{6-n} (n ≥ 3) and 1,3-C₆F₂H₄ where the easier C–H activation does not need an additional cooperating ligand, but the latter can disfavor the coordination-insertion of the olefin. Therefore a “ligandless” catalytic system is more suitable to obtain for the alkenylation products with ortho disubstituted fluoroarenes. The C–H activation of any other arene needs the help of an enabling ligand and the cooperating bipy-6-OH and phen-2-OH are suitable for this transformation.

Experimental Section

General Considerations

^1H , ^{13}C and ^{19}F NMR spectra were recorded on Bruker AV-400 or Agilent MR-500 spectrometers at the LTI-UVa. Chemical shifts (in δ units, ppm) were referenced to SiMe_4 (^1H and ^{13}C) and CFCl_3 (^{19}F). Homonuclear (^1H -COSY) and heteronuclear (^1H - ^{13}C HSQC and HMBC) experiments were used to help with the signal assignments. Solvents were dried using a solvent purification system SPS PS-MD-5 or distilled from appropriate drying agents under nitrogen prior to use and stored over 3 Å or 4 Å molecular sieves. $[\text{Pd}(\text{OAc})_2]$, N-acetylglycine, 2,2'-bipyridine, 1,10-phenanthroline, 6-methyl-2(1*H*)-pyridinone, the arenes and the alkenes used are commercially available and were used as received unless otherwise indicated. $[\text{Pd}(\text{bipy}-6\text{-OH})\text{Br}(\text{C}_6\text{F}_5)]$ (**18**),^[38] $(\text{NBu}_4)_2[\text{Pd}(\text{bipy}-6\text{-O})\text{Br}(\text{C}_6\text{F}_5)]$ (**21**),^[38] $[\text{PdBr}(\text{CH}_3\text{CN})_2(\text{C}_6\text{F}_5)]$,^[60] $(\text{NBu}_4)_2[\text{Pd}_2(\mu\text{-Br})_2\text{Br}_2(\text{C}_6\text{F}_5)_2]$,^[61] $[\text{2,2'}$ -bipyridin]-6(1*H*)-one (bipy-6-OH),^[62] 1,10-phenanthroline-2(1*H*)-one (phen-2-OH),^[63] 1,10-phenanthroline-4(1*H*)-one (phen-4-OH),^[64] $[\text{2,2'}$ -bipyridin]-4(1*H*)-one (bipy-4-OH),^[65,66] 6-methoxy-2,2'-bipyridine (bipy-6-OMe),^[62] and $\text{C}_6\text{F}_5\text{D}$,^[54] were prepared according to the procedures in the literature.

Catalytic Reactions

General procedure A: Oxidative Heck reaction of pentafluorobenzene. $[\text{Pd}(\text{OAc})_2]$ (7.65 mg, 0.034 mmol), and sodium molybdate dihydrate (8.25 mg, 0.034 mmol) were introduced in a Schlenk tube with a screw cap in an oxygen atmosphere. Then, $\text{C}_6\text{F}_5\text{H}$ (94 μL , 0.853 mmol), *tert*-butyl acrylate (50 μL , 0.341 mmol), dodecane (40 μL , 0.176 mmol) as internal standard and N,N-dimethylacetamide (3 mL) were added. Oxygen was bubbled through the mixture (5 min) and the vessel was closed. The mixture was heated in a bath at 120 °C for 6 h. The yield of the reaction was checked by ^{19}F and ^1H NMR of the crude mixture. N,N-dimethylacetamide was then removed under vacuum and n-hexane was added to the residue to extract the product. The suspension was filtered and the filtrate was evaporated to dryness obtaining an oily residue. Finally, the product was purified by column chromatography using silica gel and EtOAc: hexane=1:50 as eluent. The product was obtained as a colorless oil. Yield 90 mg (88%). The reaction can also be carried out using 5 mol% of $[\text{Pd}(\text{OAc})_2]$ (0.017 mmol).

Compound **1b** was obtained following the same procedure. The other tetra-, tri- and 1,3-di-fluorobenzenes can be olefinated in the same way using 2.5 or 5 equivalents of the fluoroarene and sometimes longer reaction times (Table 2).

General procedure B: Oxidative Heck reaction of arenes using [2,2'-bipyridin]-6(1*H*)-one. $[\text{Pd}(\text{OAc})_2]$ (3.82 mg, 0.017 mmol), $[\text{2,2'}$ -bipyridin]-6(1*H*)-one (bipy-6-OH, 2.93 mg, 0.017 mmol) and sodium molybdate dihydrate (8.25 mg, 0.034 mmol) were introduced in a Schlenk tube with a screw cap in an oxygen atmosphere. Then, the arene (1.5 mL), *tert*-Butyl acrylate (50 μL , 0.341 mmol), dodecane (40 μL , 0.176 mmol) as internal standard, and N,N-dimethylacetamide (1.5 mL) were added. Oxygen was bubbled through the mixture (5 min) and the vessel was closed. The mixture was heated in a bath at 120 °C for 6–24 h. The yield of the reaction was checked by ^{19}F and ^1H NMR of the crude mixture. N,N-dimeth-

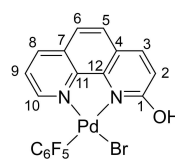
ylacetamide was then removed under vacuum and n-hexane was added to the residue to extract the product. The suspension was filtered and the filtrate was evaporated to dryness obtaining an oily residue. Finally, the product was purified by column chromatography. All the products depicted in Scheme 4 can be obtained following this procedure.

Purification details, complete characterization data and spectra for all the compounds can be found in the Supporting Information.

Synthesis of Palladium Complexes

$[\text{Pd}(\text{phen}-2\text{-OH})\text{Br}(\text{C}_6\text{F}_5)]$ (19**).** 1,10-phen-2(1*H*)-one (71 mg, 0.364 mmol) was added to a solution of $(\text{NBu}_4)_2[\text{Pd}_2(\mu\text{-Br})_2\text{Br}_2(\text{C}_6\text{F}_5)_2]$ (0.245 g, 0.181 mmol) in 20 mL of acetone. The mixture was stirred at room temperature for 2 h. During this time the orange solution became lighter and also an abundant precipitate was observed. The solvent was evaporated to c.a 5 mL and cold EtOH (10 mL) was added to the suspension. The yellow solid obtained was filtered, washed with cold EtOH (3 \times 5 mL) and air-dried. Yield: 0.16 g (80%). ^1H NMR (499.73 MHz, δ , $(\text{CD}_3)_2\text{CO}$): 11.61 (br, 1H, OH), 8.90 (d, $J=8.3$ Hz, 1H, H^{10}), 8.77 (d, $J=8.8$ Hz, 1H, H^3), 8.23 (m, 2H, H^6 , H^8), 8.13 (d, $J=8.7$ Hz, 1H, H^5), 7.86 (dd, $J=8.3$, 5.3 Hz, 1H, H^9), 7.46 (d, $J=8.8$ Hz, 1H, H^2). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.67 MHz, δ , $(\text{CD}_3)_2\text{CO}$): 166.8 (C^1), 151.7 (C^8), 146.5 (C^{12}), 143.2 (C^{11}), 142.6 (C^3), 140.1 (C^7), 139.9 (C^{10}), 130.8 (C^4), 127.9 (C^6), 125.3 (C^9), 124.6 (C^5), 117.0 (C^2). * ^{19}F NMR (470.17 MHz, δ , $(\text{CD}_3)_2\text{CO}$): -119.72 (m, 2F, F_{ortho}), -162.01 (t, $J=19.7$ Hz, 1F, F_{para}), -164.77 (m, 2F, F_{meta}). IR (neat, cm^{-1}): $\nu(\text{C}_6\text{F}_5)$ (1507, 1462, 1063, 950, 793); $\nu(\text{OH}, \text{st})$ 3031. Anal. Calcd for $\text{C}_{18}\text{H}_8\text{N}_2\text{F}_5\text{BrPd}$: C, 39.34%; H, 1.47%; N, 5.10%. Found: C, 39.15%; H, 1.21%; N, 5.53%.

*The ^{13}C signals for the C_6F_5 group, heavily coupled to ^{19}F , could not be observed due to the low solubility of this complex. The stereochemistry of **19** could not be determined as the ^1H - ^{19}F HOESY NMR experiments were inconclusive due to the low solubility of the complex; it is tentatively assigned by analogy to complex **18** bearing the similar bipy-6-OH ligand.



$[\text{Pd}_2(\text{C}_6\text{F}_5)_2(\text{CH}_3\text{CN})_2(\mu\text{-OAc})]$ (20**).** A solution of complex $[\text{PdBr}(\text{CH}_3\text{CN})_2(\text{C}_6\text{F}_5)]$ (145 mg, 0.33 mmol) in CH_3CN (3 mL) was added to a solution of AgOAc (55 mg, 0.33 mmol) in 5 mL of CH_3CN . The mixture was stirred at room temperature for 2 h protected from light. During this time an abundant precipitate was observed which was filtered. The filtrate was evaporated to dryness and diethyl ether (3 mL) was added. The yellow solid obtained was filtered, washed with ether (2 \times 3 mL) and air-dried. Yield: 0.11 g (88%). ^1H NMR (499.73 MHz, δ , CDCl_3): 2.30 (s, 6H, COOCH_3), 1.89 (s, 6H, NCCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.67 MHz, δ , CDCl_3): 183.5 (COOCH_3), 148.7 (dm, $^1J_{\text{C-F}}=233.8$ Hz, C_{ortho}), 138.3 (dm, $^1J_{\text{C-F}}=245.9$ Hz, C_{para}), 135.2 (dm, $^1J_{\text{C-F}}=252.5$ Hz, C_{meta}), 120.3 (NCCH_3 , C^2), 97.4 (d, $^2J_{\text{C-F}}=$

42.2 Hz, C_{ipso}), 23.3 (COOCH₃), 3.2 (NCCH₃). ¹⁹F NMR (470.17 MHz, δ , CDCl₃): -121.74 (m, 2F, F_{ortho}), -159.33 (t, $J=20$ Hz, 1F, F_{para}), -164.09 (m, 2F, F_{meta}). Anal. Calcd for C₂₀H₁₂F₁₀N₂O₄Pd₂: C, 32.15%; H, 1.62%; N, 3.75%. Found: C, 32.10%; H, 1.41%; N, 3.75%. IR (neat, cm⁻¹): $\nu(\text{C}_6\text{F}_5)$, (1463, 1063, 959, 796, 689); $\nu(\text{CO})$, 1583; $\nu(\text{CN, st})$ 2340(s), 2313(w).

Additional experimental information, characterization data, spectra for all the compounds, details for mechanistic experiments (kinetic monitoring and stoichiometric test reactions), computational details and Cartesian coordinates for the calculated species can be found in the Supporting Information.

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