The Pd-Catalyzed Coupling of Allyl Halides and Tin Aryls: Why the Catalytic Reaction Works and the Stoichiometric Reaction Does Not

Ana C. Albéniz, Pablo Espinet,* and Blanca Martín-Ruiz[a]

Dedicated to Professor Rafael Usón on the occasion of his 75th birthday

Abstract: Arylallylpalladium complexes [Pd(5-C_6F_5-η^3-cyclohexenyl)($C_6Cl_2F_3$)-(NCMe)] (**10**) and [Pd_2(μ-$C_6Cl_2F_3$)$_2$(5-C_6F_5-1,3-η^3-cyclohexenyl)$_2$] (**13**) have been synthesized. Complex **13** is an example of a rare class of metal complexes with aryl bridges and its X-ray crystal diffraction structure has been determined. These arylallylpalladium complexes are involved in the coupling of Bu_3SnRf (**1**, Rf = dichlorotrifluorophenyl) and [Pd_2(μ-Br)$_2$(5-C_6F_5-1,3-η^3-cyclohexenyl)$_2$] (**2**); complex **10** has been detected in the course of the stoichiometric coupling reaction in acetonitrile. Decomposition experiments of **10** and **13** in different conditions, and comparison with the reactions of **1** and **2**, allow us to determine that reductive elimination does not occur in the absence of additives. *p*-Benzoquinone coordinates to Pd to give complex **15** and promotes reductive elimination to give the coupling products selectively. The outcome of the coupling reaction is controlled by the reductive elimination step, but the overall rate is controlled by the faster preequilibrium, which determines the concentration of **10** or **13**. Palladium-catalyzed coupling of allyl halides and tin aryls works better than the stoichiometric allyl – aryl reductive coupling on isolated allylarylpalladium complexes, because they benefit from the presence in the solution of substrate allylic halides acting as electron-withdrawing olefins and promoting reductive elimination. More efficient allyl – aryl couplings, whether stoichiometric or catalytic, can be achieved upon addition of *p*-benzoquinone to the reaction mixture in a noncoordinating solvent.

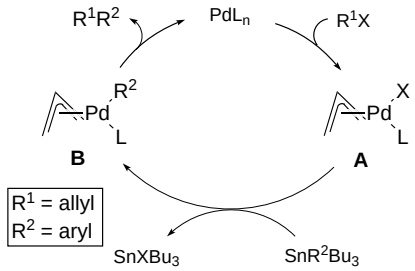
Keywords: allyl ligands · bridging aryls · C–C coupling · intermediates · palladium · reductive elimination

Introduction

Transition-metal-mediated or -catalyzed C–C coupling reactions are very important in the construction of organic molecules. The reactions of organic electrophiles (organic halides, triflates, etc.) with organometallic derivatives (particularly of Mg, Zn, Cu, Sn, Si, or B) catalyzed by palladium complexes are widely used.[1, 2] The coupling reactions that use organotin derivatives as the nucleophile source (Stille reaction) are often chosen because of the stability of these reagents and the variety of functional groups that can be tolerated.[2] Compared with their extensive synthetic application, mechanistic studies on these processes are still scarce.

The mechanism of the coupling of aryl halides or triflates with aryl- or vinyltin derivatives has been studied in detail, and we have shown that the rate determining step for the process can be either the transmetallation of the organic group from tin to palladium or the oxidative addition, depending on the exact circumstances of the reaction.[3]

On the other hand, coupling involving allylic electrophiles is expected to proceed by a similar route (oxidative addition to give **A**, transmetallation to give **B**, and reductive elimination of the coupling product), which is represented in a simplified way in Scheme 1. In this case, however, the reductive elimination step from a putative allylarylpalladium complex (**B**, Scheme 1), might become rate determining, since the C–C allyl – aryl coupling is expected to be slower than those of aryl – aryl or vinyl – aryl.[4]



Scheme 1. Simplified mechanism for the aryl – allyl coupling.

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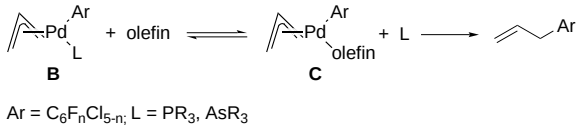
In fact Schwartz and co-workers have reported that the coupling of allylic halides and allylic organometallics does not proceed unless electron-withdrawing olefins are added. They have attributed this to the allyl–allyl coupling (from a putative, reversibly formed, bis(allyl)palladium intermediate) being extremely slow, while it is accelerated by the addition of π-acidic ligands, particularly electron-withdrawing olefins such as maleic anhydride.[5–8] In this respect it is also interesting to note the detection by NMR spectroscopy of a bisallyl complex [Pd(η^3-C_3H_5)(η^1-$CH_2CH{=}CHPh$)(PPh_3)] in the reaction of allyltributyltin with a phenylallyl palladium chloride dimer.[9] The reductive elimination in allylarylpalladium complexes of type **B** has been carefully studied by Kurosawa and co-workers, and they also noted this promoting effect of electron-withdrawing olefins.[10–13] Kinetic studies supported by theoretical work suggest that the reductive elimination occurs in an η^3-allylpalladium complex with a coordinated olefin (**C**), which was detected by NMR spectroscopy at low temperature (Scheme 2).[13] These results have been used to improve some catalytic coupling reactions by adding electron withdrawing olefins, often maleic anhydride.[5, 14, 15]



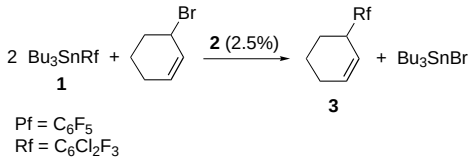
Scheme 2. Promotion of reductive elimination in some arylallylpalladium derivatives.

Fluoroaryls have proved to be useful moieties for the study of reaction mechanisms and the detailed analysis of reaction mixtures.[3, 16, 17] In this paper, by using fluorinated aryl derivatives we have been able to detect complex **B** (Scheme 1) in the course of a coupling reaction, as well as some other species involved in the catalytic cycle or closely related to it. We examine in detail the stoichiometric and catalytic coupling of cyclohexen-3-yl derivatives and tributyl(dichlotrifluorophenyl)tin, analyzing the pathways that compete with it, and finding the conditions that make the coupling efficient. Altogether, a clear picture of the coupling reaction and the competing processes is obtained.

Results and Discussion

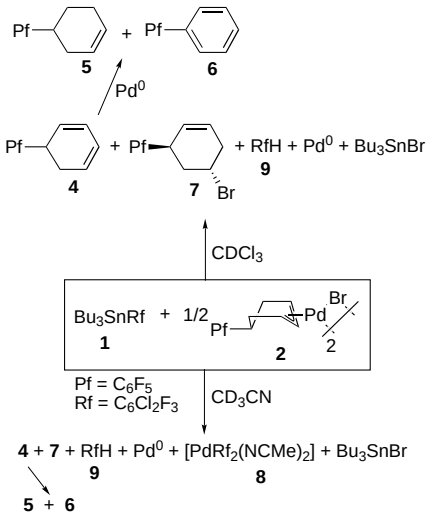
Reactions of cyclohexenyl derivatives with Bu_3SnRf (Rf = $C_6Cl_2F_3$): The reaction of cyclohexenyl bromide and Bu_3SnRf (**1**, Rf = dichlorotrifluorophenyl) in chloroform at 50 °C, catalyzed by 2.5% of the η^3-allyl palladium complex di-μ-bromobis(5-pentafluorophenyl-1-3-η^3-cyclohexenyl)-dipalladium(II) (**2**),[17] slowly gave the coupling product 3-(dichlorotrifluorophenyl)-cylohexene (**3**) (Scheme 3, 46% yield after 14 days).

In order to study the transformation from **A** to the coupling product (this includes the transmetallation step plus the reductive elimination step, and will be referred to hence from as "coupling process") we carried out the stoichiometric



Scheme 3. Coupling of cyclohexenyl bromide and Bu_3SnRf (**1**).

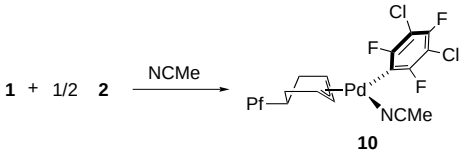
model reaction of **1** with the palladium allyl **2** in chloroform or acetonitrile at 50 °C (Scheme 4 and Table 1, entries 1, 2). The presence of two different fluorinated groups in both substrates allowed us to monitor the reaction by ^{19}F NMR spectroscopy and, together with ^1H NMR experiments, identify all the products of the reaction. Unexpectedly no coupling product was obtained, but several other compounds



Scheme 4. Decomposition products for the reaction of **1** and **2** in different solvents.

were observed and identified. Control experiments showed that the decomposition occurs only when both reagents are present and does not arise from either reagent alone. Under the same conditions used for the attempted stoichiometric couplings ($CDCl_3$, 50 °C, 1 day; CD_3CN, 50 °C, 2 h) **1** or **2** by themselves remained unchanged. The decomposition reaction was not affected by oxygen or by the radical-trap galvinoxyl.

The stoichiometric reaction was also carried out in acetonitrile at a lower temperature (30 °C) and monitored by ^{19}F NMR spectroscopy. After 4 h, 30% of the starting material had converted to a new complex, which was identified as (5-pentafluorophenyl-1-3-η^3-cyclohexenyl)(dichlorotrifluorophenyl) acetonitrilepalladium(II) (**10**) (Scheme 5) and corre-



Scheme 5. Stoichiometric reaction of **1** and **2** in acetonitrile.

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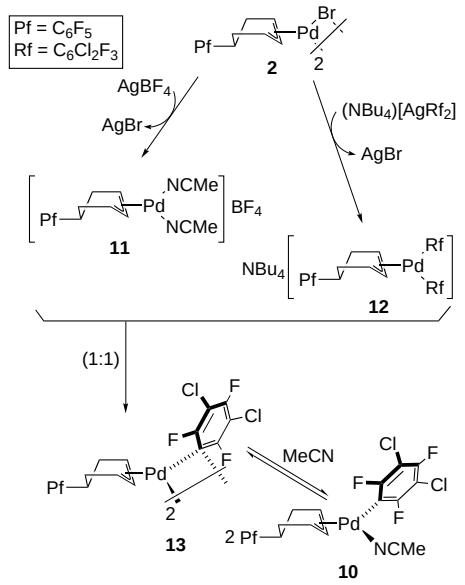
Table 1. Coupling and decomposition reactions of **1** + **2** and intermediates **10** and **13**.[a]

Entry	Reaction mixture	Solvent	Time	**4**	**5**	**6**	**7**	**14** (*cis* + *trans*)	**9**	**8**	Other (yield)
1	**2** + **1** (Pd:Sn = 1:1)	$CDCl_3$	6 days	6	44	34	6	–	90	–	**1** (10)
2	**2** + **1** (Pd:Sn = 1:1)	CD_3CN	2 h	5	57	26	4	–	22	49	**1** (29)
3	**13**	$CDCl_3$	13 h	–	34	66	–	–	100	–	–
4	**10**	CD_3CN	2.5 h	–	35	65	–	–	53	47	–
5	**2** + Bu_3SnBr	$CDCl_3$	1 day	–	–	–	32	–	–	–	**2** (68)
6	**2** + Bu_3SnBr	CD_3CN	2 h	–	3	–	9	–	–	–	**2** (88)
7	**13** + Bu_3SnBr	$CDCl_3$	10 min	–	–	–	–	–	–	–	**1** (100), **2** (100)
8	**10** + Bu_3SnBr	CD_3CN	10 min	4	–	–	–	–	5	-	**1** (21), **2** (22), **10** (74)
9	**2** + **1** + benzoquinone (Pd:Sn:bzq = 1:1:1)	$CDCl_3$	1 day	–	5	21	5	63 (60 + 3)	22	–	Bu_3SnRf (15)
10	**13** + benzoquinone (Pd:bzq = 1:1)	$CDCl_3$	10 min	1	–	2	–	97	3	–	–
11	**2** + **1** + benzoquinone (Pd:Sn:bzq = 1:1:20)	CD_3CN	3 h	12	–	7	2	79 (13 + 66)	1	13	**1** (7)
12	**10** + benzoquinone (Pd:bzq = 1:20)	CD_3CN	40 min	5	–	–	–	92	6	2	**11** (3)
13	**10** + benzoquinone (Pd:bzq = 1:1)	CD_3CN	40 min	67	–	7	3–	20	67	13	
14	**2** + benzoquinone (Pd:bzq = 1:20)	CD_3CN	2.5 h	–	–	–	31		–	–	*cis*-**2** (50), *trans*-**2** (19)
15	**2** + benzoquinone (Pd:bzq = 1:1)	$CDCl_3$	1 day	–	–	–	–		–	–	**2** (100)

[a] All the reactions were carried out at 50 °C. The yields given (%) were determined by integration of ^{19}F NMR signals and represent the distribution of Pf and Rf in the compounds independently (total Pf = 100 %; total Rf = 100 %).

sponds to the transmetallation intermediate **B** in Schemes 1 and 2 above. Complex **10** is also observed, but does not accumulate when the reaction is carried out at 50 °C. An independent synthesis of this compound and a study of its decomposition were carried out.

Synthesis and decomposition experiments of plausible transmetallation intermediates: The cationic Pd-allyl **11** and the allyl bisarylpalladium complex **12** were prepared from **2** by reaction with the corresponding silver salt, as summarized in Scheme 6. The reaction of **11** and **12** in acetone produces the



Scheme 6. Synthesis of **13** and **10**.

orange aryl-bridged **13**. Acetonitrile as solvent splits these bridges to give colorless **10** in solution, but evaporation and crystallization drives the equilibrium back to **13**.

The X-ray crystal structure of **13** shows a centrosymmetric molecule with both palladium atoms and bridging ipso carbons in the same plane and the dichlorotrifluoroaryl rings perpendicular to that plane (Figure 1). Selected bond lengths

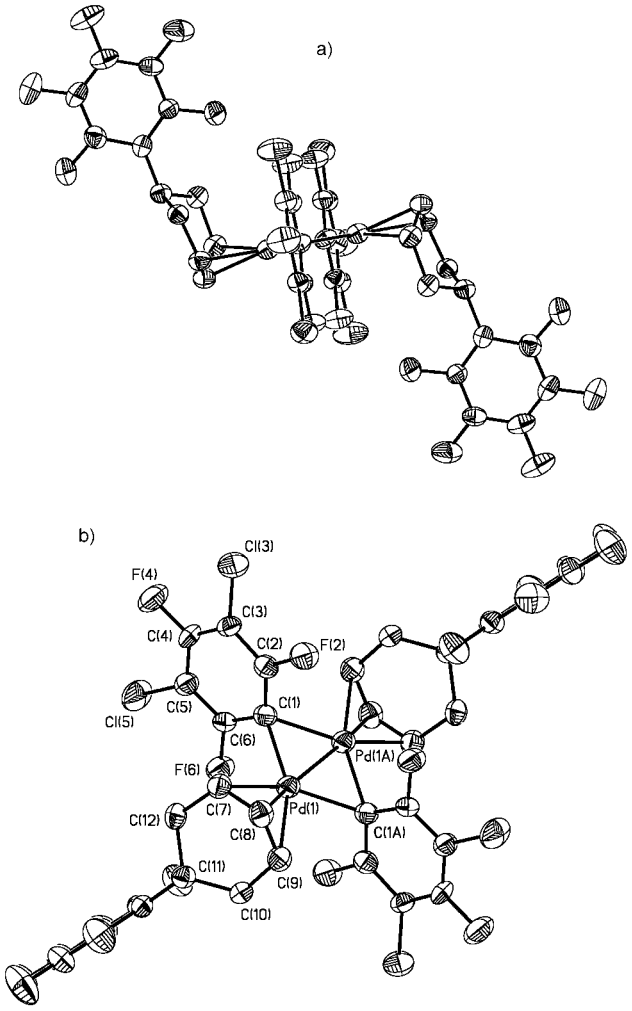


Figure 1. Ortep drawing of complex **13**, showing the *trans* arrangement of both allyl moieties in the dimer (a) and two views of the aryl bridges (a and b).

and angles are collected in Table 2. Each aryl bridge is unsymmetrical with two slightly different Pd–C_{ipso} bond lengths (2.195 and 2.242 Å). This asymmetry and bond lengths

Table 2. Selected bond lengths [Å] and angles [°] for complex **13**.

Pd(1)−C(8)	2.100(7)	C(1)-Pd(1)-C(1A)	105.38(19)
Pd(1)−C(7)	2.129(6)	C(1)-Pd(1)-Pd(1A)	53.47(16)
Pd(1)−C(9)	2.176(6)	Pd(1)-C(1)-Pd(1A)	74.62(19)
Pd(1)−C(1)	2.195(6)	C(1A)-Pd(1)-Pd(1A)	51.90(16)
Pd(1)−C(1A)	2.242(6)	C(9)-C(8)-C(7)	115.9(6)
Pd(1)−Pd(1A)	2.6897(11)	C(8)-C(9)-C(10)	120.4(6)
C(7)−C(8)	1.393(8)	C(9)-C(10)-C(11)	110.5(5)
C(8)−C(9)	1.389(8)	C(10)-C(11)-C(12)	111.3(5)
C(9)−C(10)	1.514(8)	C(6)-C(1)-C(2)	114.8(6)
C(10)−C(11)	1.525(8)	C(1)-C(2)-C(3)	123.2(6)
C(11)−C(12)	1.534(8)	C(4)-C(3)-C(2)	118.0(6)
C(7)−C(12)	1.510(8)	C(3)-C(4)-C(5)	122.0(6)
C(1)−C(6)	1.377(9)	C(6)-C(5)-C(4)	116.9(6)
C(1)−C(2)	1.381(8)	C(5)-C(6)-C(1)	125.0(6)
C(2)−C(3)	1.392(8)		
C(3)−C(4)	1.364(9)		
C(4)−C(5)	1.379(8)		
C(5)−C(6)	1.373(8)		

in the bridges are similar to those found in the structure of $[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]^{2-}$.[18] However, in contrast with **13**, the Pt coordination planes in the Pt-dimer form a dihedral angle of 151.9° and the bridging aryl rings are not parallel to each other. The cyclohexenyl moieties in **13** have a *trans* arrangement and a pseudoboat conformation with the bulky pentafluorophenyl groups in the equatorial position. The Pd-allyl bond lengths found here are comparable to other palladium η^3-cyclohexenyl structures,[17, 19] but the allyl moiety is asymmetrically coordinated: a larger Pd−C(allyl) bond length *trans* to the shorter Pd-C(bridging aryl) bond is found (Pd−C(9), 2.176 Å versus Pd−C(7), 2.129 Å). The short Pd−Pd bond length in the dimer (2.6897 Å) suggests some degree of metal–metal interaction. A search in the Cambridge Crystalographic Database for the structures reported with Pd−Pd bonds gives an average Pd−Pd length of 2.766 Å, with most structures within the range 2.575 to 2.775 Å.[20] The Pd−Pd bond length in **13** is within this range, and is shorter than found in the metal (2.75 Å).[21] A short Pt−Pt bond length was similarly found in $[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]^{2-}$.[18] The analogous $[Pd_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]^{2-}$ is the only palladium complex with pentafluorophenyl bridges reported in the literature, but its crystal structure has not been reported.[22]

The ^{19}F and ^1H NMR spectra in $CDCl_3$ (Figure 2) show that **13** gives a 1:1 mixture of two isomers, corresponding to the *cis* and *trans* arrangements of two allyl groups in a dimer. The bridging nature of the two Rf groups is revealed by the remarkable downfield shift of their F_{ortho} signals.[18, 22] When a solution of **13** is warmed to 50 °C in $CDCl_3$ the signals in the ^{19}F NMR spectrum become broad, indicating slow interconversion of the two isomers, probably by bridge splitting and reforming, as observed for **2** and for related halogen-bridged allyl complexes.[17, 23] The dimeric structure of **13** is maintained in solvents of low to moderate coordination ability ($CHCl_3$, CH_2Cl_2, acetone, and Et_2O), but acetonitrile splits the bridges to give **10**, as stated above.

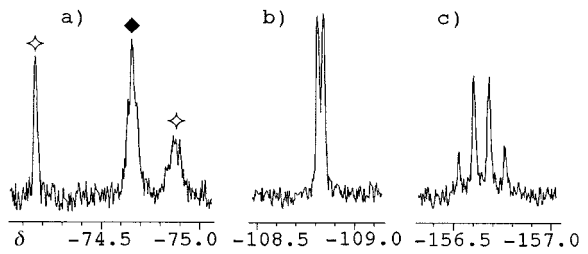
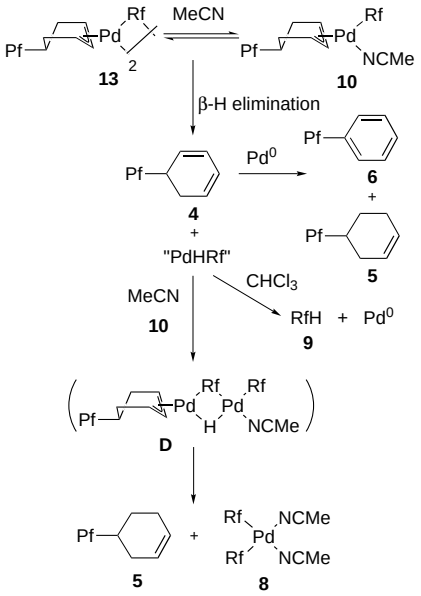


Figure 2. ^{19}F NMR spectrum of the mixture of *cis* and *trans* isomers (1:1) of complex **13** in $CDCl_3$: a) F_{ortho} of bridging $C_6Cl_2F_3$ (◇ *cis*; ◆ *trans*) ; b) F_{para} of bridging $C_6Cl_2F_3$; c) F_{para} of C_6F_5.

Complex **13** decomposes in $CDCl_3$ or in CD_3CN (where it gives **10**) at 50 °C to give the same products obtained in the reactions of Bu_3SnRf (**1**) and **2**. The results of these experiments are collected in Table 1 (entries 3, 4). Scheme 7



Scheme 7. Decomposition routes for complexes **10** and **13**.

illustrates the plausible pathways leading to the decomposition products observed. Three main decomposition routes can be invoked to explain the outcome of the reactions. β-H elimination in the allylic complexes is the main source of the cyclohexadienyl derivative **4** and, by disproportionation promoted by Pd^0, of 4-pentafluoro cyclohexene (**5**) and pentafluorobiphenyl (**6**).[24] Reductive elimination in the hydrido complex thus formed produces dichlorotrifluorobenzene (RfH, **9**) and Pd^0. In the coordinating acetonitrile "PdHRf" is somewhat stabilized, enough for it to react in part with the starting complex and produce $[Pd(Rf)_2(NCMe)_2]$ (**8**) by group exchange via a putative intermediate **D**.[25] This rearrangement is not observed in $CDCl_3$, where decomposition of "PdHRf" dominates.

The agreement between the results of the decomposition of **13** or **10** (entries 3 and 4, Table 1) and the outcome of the coupling process from **1** and **2** (entries 1 and 2, Table 1) is good. The major decomposition products of the Pf-substituted ($Pf = C_6F_5$) moiety arise from β-H elimination (the actual ratio between **4**, **5**, and **6** depends on the catalytic activity and features of the Pd-black generated). RfH (**9**) is the main Rf product in the reactions in $CDCl_3$, and both RfH and **8** are formed in CD_3CN. This supports the formation of arylallyl-

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palladium complexes (**10** and **13**) in the stoichiometric reaction with the tin derivative.

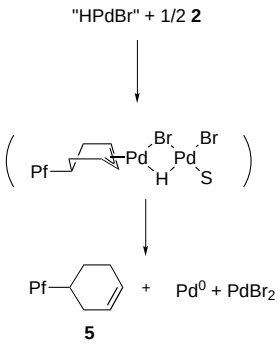
Thus, when β-H elimination is possible, as is the case with the cyclohexenyl moiety used in this work and of many allylic derivatives, this is the dominant decomposition pathway of the intermediate allylaryl complex. Interestingly no β-H elimination occurs for the starting complex **2** or the cationic **11** when warmed in solution. We suggest that this allyl moiety can undergo easy β-H elimination only when it becomes η^1-bonded; this implies decoordination of the double bond, which should be easier in **10** or **13**. It is now well established that dissociative mechanisms in Pt and Pd are greatly facilitated in complexes containing two soft carbon donors that make the Pd center electron rich (such as **10** or **13**), compared with halo complexes (such as **2**) or cationic complexes (such as **11**).[26]

Small differences are also observed between the results of the decomposition of **13** or **10** and the coupling process from **1** and **2** . First of all, the small amount of **7** observed in entries 1 and 2 (Table 1) is attributed to the reaction of the byproduct Bu_3SnBr and starting **2**, which was independently tested (see entries 5 and 6, Table 1).

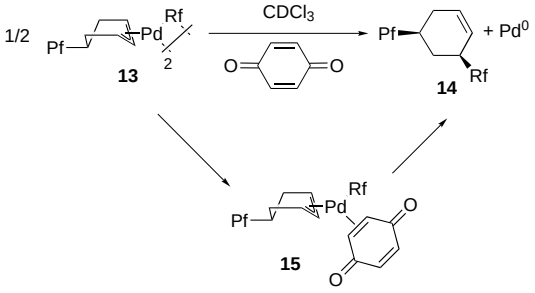
Another remarkable point is that the reaction rates for the decomposition of **13** or **10** and for the coupling process of **1** and **2** are similar in CD_3CN (entries 2 and 4), but very different in $CDCl_3$ (entries 1 and 3). We have observed that the transmetallation step is reversible and the equilibrium **1**+**2**$\rightleftharpoons$**13**+$SnBu_3Br$ is shifted almost completely to the left in $CDCl_3$. When **13** is mixed with Bu_3SnBr at 50 °C for 10 minutes apparently total conversion to **1** and **2** occurs (entry 7, Table 1). However, when **13** is dissolved in CD_3CN only about 20 % is converted to **1** and **2** (entry 8, Table 1), showing that the equilibrium **1**+**2**$\rightleftharpoons$**10**+$SnBu_3Br$ is displaced to the right. Conversely, when **1** and **2** are mixed, a high concentration of **10** in acetonitrile is obtained, whereas only a small concentration of **13** is formed in chloroform. This leads to comparable reaction times for **1**+**2** and for **10** in acetonitrile, but not in chloroform in which **13** is much less abundant when formed from **1**+**2** than when added as a pure substance.

Finally, some Bu_3SnRf (**1**) remains unreacted in the reactions of **1** and **2** when all the palladium complex **2** has been consumed. We see that the byproduct Bu_3SnBr promotes the decomposition of **2** to some extent. In addition, the "PdHBr" produced in the reaction can lead to additional consumption of **2** according to Scheme 8. This seems to be supported by the fact that the excess of **1** (or rather the defect of **2** because of its consumption in side reactions) is higher in MeCN in which "PdHBr" is better stabilized.

Promotion of the reductive elimination step: In order to favor the formation of the coupling product **14** (Scheme 9) from **13** or **10**, the rate of the reductive elimination step must be increased to surpass the rate of β-H elimination. Electron-withdrawing olefins, such as maleic anhydride or allylic chlorides, have been shown to speed up this reaction.[5–8, 11a–14, 27] Oxidants have also been tried, following the increase in the reductive elimination rate upon oxidation obtained for some dialkyliron complexes,[28] although they seem to be less efficient for palladium allyl complexes.[6] We



Scheme 8. Mechanism for decomposition of **2** by palladium hydrido species.



Scheme 9. Role of *p*-benzoquinone in the formation of the coupling product **14**.

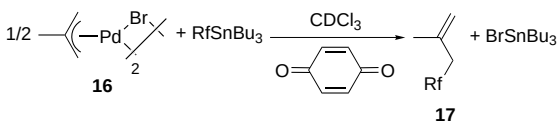
find that *p*-benzoquinone has the highest effect on the reductive elimination step for **13** and **10**. Maleic anhydride and oxidants such as Ag^+ or $[MoO_2Cl_2(dmso)_2]$ were ineffective giving RfH (**9**) as the main product. The reactions of **10** and **13** with *p*-benzoquinone are given in Table 1 (entries 10, 12, and 13). When complex **13** was warmed in $CDCl_3$ in the presence of *p*-benzoquinone (Pd:benzoquinone = 1:1) the coupling product **14** was obtained almost quantitatively. Excess of *p*-benzoquinone was needed to obtain the same effect when **10** was decomposed in CD_3CN. This suggests that the reductive elimination occurs in an allylarylpalladium *p*-benzoquinone complex, **15**, which is more easily obtained in chloroform than in the coordinating solvent acetonitrile. In fact, complex **15** was detected upon addition of *p*-benzoquinone to a solution of complex **13** in chloroform at 243 K. This complex **15** shows the characteristic ^{19}F pattern for a non-rotating Rf group coordinated to Pd ($\delta = -89.8$ and -92.4 for the inequivalent F_{ortho}) and the corresponding signals for the Pf group. It can also be detected in CD_3CN at room temperature when **10** and an excess of *p*-benzoquinone are mixed. When a solution containing equimolar amounts of **10** and *p*-benzoquinone in a mixture of CH_2Cl_2/CH_3CN at low temperature was evaporated to dryness, and the residue was dissolved in $CDCl_3$ at 243 K, the amount of **15** formed was higher and made full NMR characterization possible. The *p*-benzoquinone has two protons that display an upfield shift ($\delta = 5.47$ and 5.43), typical of a coordinated double bond, compared with the other two on a noncoordinated double bond ($\delta = 6.52$ and 6.46). Upon increase of the temperature, **15** decomposed cleanly to the coupling product **14**.

Table 1 also shows the effect of the use of *p*-benzoquinone in the stoichiometric coupling process of the **1** and **2** (entries 9

and 11). Again, the coupling product **14** could be obtained in these conditions and the analogies observed between these couplings and the decomposition of **10** or **13** are evident. There are noteworthy differences, though. First, the reaction of **1** and **2** in acetonitrile in the presence of *p*-benzoquinone gives a diasteromeric mixture of the coupling products *cis* and *trans*-**14**. The higher the amount of *p*-benzoquinone used, the more *trans*-**14** is obtained. We have observed in a control experiment (entry 14, Table 1) that the presence of *p*-benzoquinone in solutions of complex **2** in acetonitrile promotes reductive elimination to give 3-bromo-5-pentafluorophenylcylohexene (**7**) and, by oxidative addition of this compound in a nonsteroselective way,[29] the diastereomeric allyl derivative *trans*-**2** with Pf and Pd on different sides of the cyclohexenyl ring. This is favored, since *p*-benzoquinone is a ligand capable of stabilizing Pd^0.[30] Thus, **2** and *p*-benzoquinone (Pd:benzoquinone = 1:20) in CD_3CN gives 31% of **7** and 19% of *trans*-**2** in 2.5 h at 50 °C (entry 14, Table 1). This is not observed when **2** and *p*-benzoquinone (1:1 ratio) are mixed in chloroform (entry 15, Table 1). The coupling product obtained in this solvent is mostly *cis*-**14** (60%), and the small amount of *trans*-**14** found (3%, entry 9, Table 1) could originate from the formation of **7** promoted, as was mentioned before, by the presence of Bu_3SnBr (entries 1 and 5, Table 1).

The rate differences observed before for the reaction of **1**+**2** and the decomposition of **10** (in CD_3CN, same order of rate) or **13** (in $CDCl_3$, very different rates) in the absence of *p*-benzoquinone, are also observed here (cf. entries 9–12, Table 1). This suggests that the coupling, although considerably accelerated by *p*-benzoquinone and faster than other decomposition pathways, is still slower than the transmetallation. For this reason its rate is controlled by the faster preequilibrium which determines the concentration of **10** or **13**.

The effect of *p*-benzoquinone was also tested by reacting di-μ-bromobis(2-methyl-1-3-η^3-allyl)dipalladium(II) (**16**), which cannot undergo β-H elimination side reactions. When **16** was warmed with Bu_3SnRf (**1**) in chloroform solution at 50 °C for six days, only 8% of the coupling product 3-(dichlorotrifluorophenyl)-2-methylpropene (**17**) was obtained. However, when the reaction was carried out in the same conditions in the presence of *p*-benzoquinone (Pd:benzoquinone = 1:1), quantitative formation of **17** was observed after one day (Scheme 10).



16 **17**

Scheme 10. Reaction of **16** with Bu_3SnRf.

Catalytic reactions: The information obtained was used to improve the coupling of cyclohexenyl bromide and Bu_3SnRf (**1**) catalyzed by the allylic complex **2** (Scheme 3). Table 3 collects the results obtained when the reaction was carried out with and without additives. It is clear that the optimal conditions are met by addition of *p*-benzoquinone in a noncoordinating solvent such as chloroform, in which **3** can be obtained in 92% yield. *p*-Benzoquinone has no perceptible effect in a coordinating solvent like acetonitrile. Maleic anhydride has a detrimental effect, as was observed before for the decomposition of complex **13**. These observations parallel the results just described in the sections above. Table 3 also shows the analogous results obtained for the coupling of allyl chloride and **1**. Again, the yield of coupling product 3-(dichlorotrifluorophenyl)propene (**18**) is higher when *p*-benzoquinone is used.

Conclusion

When used in C–C coupling reactions, allylic derivatives show distinct features that have been studied in detail by analyzing stoichiometric couplings between haloaryltin derivatives and allylpalladium complexes along with the synthesis of arylallylpalladium derivatives involved in the reaction. Transmetallation from tin allyls to arylPd complexes reversibly gives arylallylpalladium derivatives, such as **10** or **13**. The following step, reductive elimination, is slow and controls the reaction outcome, but its rate is, in turn, controlled by the actual concentration of the arylallylpalladium complex **10** or **13**. Furthermore, in order to produce an efficient coupling, coordination of a promoter of reductive elimination such as *p*-benzoquinone, an electron-withdrawing olefin, is very effective. Both the concentration of the arylallylpalladium complex (in our case **10** or **13**) and the ease of coordination of the promoter will depend on the coordinating ability of the solvent. In the absence of a good promoter, β-H elimination and group exchange are the main decomposition pathways observed.

Finally, since we have shown that **10** or **13** do not give the reductive elimination compound in the absence of a promoter, the noticeable amount of coupling product **3** observed in

Table 3. Catalytic coupling of allyl bromides with **1**.

Entry	Reaction mixture	Solvent	Additive	time [days][a]	Coupling product (%)	Other Rf products (%)
1	**1** + cyclohexenyl bromide	$CDCl_3$	–	14	**3** (46)	**9** (54)
2	**1** + cyclohexenyl bromide	$CDCl_3$	benzoquinone	4	**3** (92)	**9** (8)
3	**1** + cyclohexenyl bromide	$CDCl_3$	maleic anhydride	9	**3** (38)	**9** (62)
4	**1** + cyclohexenyl bromide	CD_3CN	–	1	**3** (56)	**9** (34), **8** (2), **1** (8)
5	**1** + allyl chloride	$CDCl_3$	–	2	**18** (70)	**9** (4), **1** (18)
6	**1** + allyl chloride	$CDCl_3$	benzoquinone	1	**18** (89)	**1** (9)

[a] Time needed for completion of the reaction.

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the catalytic reactions (46%) has to be attributed to the presence of the allylic substrate, an electron-withdrawing olefin itself.[12] As can be seen in Table 3, allyl chloride, being a better ligand and a more electron-withdrawing olefin than cyclohexenyl bromide, promotes reductive elimination more efficiently, and the catalytic reaction in the absence of *p*-benzoquinone gives higher yield of coupling product. Nonetheless the catalytic coupling still benefits from the addition of *p*-benzoquinone.

Experimental Section

General: ^{19}F and ^{1}H NMR spectra were recorded on Bruker AC300 and ARX300 instruments. Chemical shifts are reported in δ units (ppm) downfield from Me_4Si for ^{1}H and from $CFCl_3$ for ^{19}F. The spectra were recorded at 293 K except when noted. Carbon, nitrogen, and hydrogen analyses were carried out on a Perkin-Elmer 2400 CHN Elemental Analyzer. IR spectra were carried out using a Perkin–Elmer 883 spectrophotometer. Organic products were analyzed by using a HP-5890 gas chromatograph connected to an HP-5988 mass spectrometer at an ionizing voltage of 70 eV using a quadrupole analyzer.

The reactions involving organolithium reagents were carried out under N_2 using solvents dried by standard methods and freshly distilled. $AgBF_4$, $C_6Cl_3F_3$, allyl chloride, cyclohexenyl bromide, and additives are commercially available and were used without further purification. Compounds **6** and **9** are known, but their spectral data are given for completeness. $Bu_3SnC_6Cl_2F_3$ (**1**),[3b] (η^3-allyl)palladium bromide dimers **2**[17] and **16**,[31] and $[MoO_2Cl_2(dmso)_2]$[32] were prepared as reported in the literature.

General procedure for the stoichiometric reactions of $[Pd_2(\mu\text{-Br})_2(\eta^3\text{-allyl})_2]$ and 1: The solvent (0.5 mL) and the tin reagent **1** (0.020 mmol) were added to an NMR tube that contained $[Pd_2(\mu\text{-Br})_2(\eta^3\text{-allyl})_2]$ (0.010 mmol) and the additive (when it was used),. The mixture was placed in a preheated oil bath at 50 °C throughout the reaction time. The products were analyzed by ^{19}F and ^{1}H NMR spectroscopy, and, after elimination of the Pd^0 by filtration through activated carbon, by GC-MS. The results of the experiments carried out are collected in Table 1.

Compound 4: ^{1}H NMR (300 MHz, $CDCl_3/CD_3CN$): $\delta = 6.03/6.05$ (m, 2H; H^2, H^3), 5.93/5.90 (m,1H; H^1), 5.70/5.72 (d, $J = 9.0$ Hz, 1H; H^4), 4.10/4.08 (m, $J = 17.2$, 9.0 Hz, 1H; H^5), 2.45/2.35 (m, 1H; H^6), 2.30/2.35 (m, 1H; $H^{6'}$); ^{19}F NMR (282 MHz, $CDCl_3/CD_3CN$): $\delta = -162.94/-164.31$ (m; F_{meta}), $-157.66/-159.19$ (t; F_{para}), $-140.65/-141.20$ (m; F_{ortho}); MS: *m*/*z* (%): 246 (100) $[M]^+$, 205 (20), 181 (89), 169 (10), 123 (22), 99 (11), 77 (37), 51 (26).

Compound 5: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.75$ (m, 2H; H^1, H^2), 3.25 (tdd, $J = 11.5$, 5.3, 2.6 Hz, 1H; H^4), 2.42 (m, 1H; H^3), 2.25–2.05 (m, 4H; $H^{3'}$, H^6, $H^{6'}$, H^5), 1.85 (dm, $J = 11.5$ Hz, 1H; $H^{5'}$); ^{19}F NMR (282 MHz, $CDCl_3/CD_3CN$): $\delta = -163.22/-164.31$ (m; F_{meta}), $-158.52/-159.79$ (t; F_{para}), $-143.62/-144.03$ (m; F_{ortho}); MS: *m*/*z* (%): 248 (69) $[M]^+$, 220 (17), 194 (70), 151 (25), 143 (12), 99 (13), 67 (17), 54 (100).

Compound 6: ^{1}H NMR (300 MHz, $CDCl_3/CD_3CN$): $\delta = 7.55-7.40/7.60-7.40$ (m, 5H); ^{19}F NMR (282 MHz, $CDCl_3/CD_3CN$): $\delta = -162.65/-164.01$ (m; F_{meta}), $-156.05/-157.48$ (t; F_{para}), $-143.71/-144.36$ (m; F_{ortho}); MS: *m*/*z* (%): 244 (100) $[M]^+$, 224 (27), 205 (12), 194 (3), 192 (10), 167 (4), 123 (8), 117 (7), 93 (8), 51 (16), 50 (17).

Compound 7: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.03$ (m, $J = 9.5$ Hz, 1H; H^2), 5.90 (m, $J = 9.5$, 5.5, 2.3 Hz, 1H; H^1), 4.95 (m, 1H; H^3), 3.85 (tdd, $J = 12.1$, 5.5, 2.5 Hz, 1H; H^5), 2.62 (m, 2H; $H^{4'}$, $H^{6'}$), 2.42 (dt, $J = 18.0$, 5.5 Hz, 1H; H^6), 2.27 (d, $J = 14.0$ Hz, 1H; $H^{4'}$); ^{19}F NMR (282 MHz, $CDCl_3/CD_3CN$): $\delta = -162.55/-163.98$ (m; F_{meta} C_6F_5), $-157.07/-158.83$ (t; F_{para} C_6F_5), $-142.68/-143.32$ (m; F_{ortho} C_6F_5); MS: *m*/*z* (%): 282 (12), 247 (51) $[M-Br]^+$, 181 (100), 143 (11), 123 (10), 88 (84), 77 (26), 51 (33).

Compound 8: ^{19}F NMR (282 MHz, CD_3CN): $\delta = -119.94$ (s; F_{para} $C_6Cl_2F_3$), -89.95 (s; F_{ortho} $C_6Cl_2F_3$). These data were compared with those obtained when *cis*-$[(C_6Cl_2F_3)_2Pd(thf)_2]$[33] was dissolved in CD_3CN.

Compound 9: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.92$ (td, $^3J(H,F) = 9$ Hz, $^5J(H,F) = 2$ Hz, 1H); ^{19}F NMR (282 MHz, $CDCl_3/CD_3CN$): $\delta = -111.98/-113.02$ (d, $^3J(H,F) = 9$ Hz; F_{ortho}), $-110.61/-112.44$ (s, F_{para}).

Compound *cis*-14: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.92$ (dq, $J = 10.2$, 2.4 Hz, 1H; H^2), 5.65 (br d, $J = 10.2$ Hz, 1H; H^1), 4.05 (m, 1H; H^3), 3.50 (tdd, $J = 11.5$, 5.6, 2.6 Hz, 1H; H^5), 2.55 (m, 1H; $H^{6'}$), 2.40 (m, 1H; H^4), 2.25 (m, 1H; H^6), 2.00 (dm, $J = 11.7$ Hz, 1H; $H^{4'}$); ^{1}H NMR (300 MHz, CD_3CN): $\delta = 5.91$ (dq, $J = 10.6$, 2.7 Hz, 1H; H^2), 5.67 (br d, $J = 10.6$ Hz, 1H; H^1), 4.07 (m, 1H; H^3), 3.52 (tdd, $J = 11.8$, 5.4, 2.6 Hz, 1H; H^5), 2.50 (m, 1H; $H^{6'}$), 2.32 (m, 2H; H^4, H^6), 2.03 (m, 1H; $H^{4'}$); ^{19}F NMR (282 MHz, $CDCl_3/CD_3CN$): $\delta = -162.60/-164.00$ (m; F_{meta} C_6F_5), $-157.33/-159.00$ (t; F_{para} C_6F_5), $-143.25/-143.60$ (m; F_{ortho} C_6F_5) , $-115.24/-115.40$ (s; F_{ortho} $C_6Cl_2F_3$), $-113.98/-115.70$ (s; F_{para} $C_6Cl_2F_3$); MS: *m*/*z* (%): 450 (4), 449 (3), 448 (18), 447 (4) $[M]^+$, 446 (23), 252 (54), 213 (39), 194 (53), 182 (100), 143 (32), 99 (10), 41 (8).

Compound *trans*-14: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.02$ (dq, $J = 10.3$, 2.7 Hz, 1H; H^2), 5.80 (br d, $J = 10.3$ Hz, 1H; H^1), 3.96 (m, 1H; H^3), 3.50 (tm, $J = 12.0$ Hz, 1H; H^5), 2.55 (m, 2H; H^4, H^6), 2.35 (m, 1H; $H^{6'}$), 1.90 (d, $J = 11.8$ Hz, 1H; $H^{4'}$); ^{1}H NMR (300 MHz, CD_3CN): $\delta = 6.02$ (dq, $J = 10.6$, 2.7 Hz, 1H; H^2), 5.83 (br d, $J = 10.6$ Hz, 1H; H^1), 3.98 (m, 1H; H^3), 3.45 (tdd, $J = 12.3$, 5.7, 2.7 Hz, 1H; H^5), 2.42 (m, 3H; H^4, H^6, $H^{6'}$), 1.92 (m, 1H; $H^{4'}$); ^{19}F NMR (282 MHz, $CDCl_3/CD_3CN$): $\delta = -162.60/-164.10$ (m; F_{meta} C_6F_5), $-157.47/-159.05$ (t; F_{para} C_6F_5), $-142.95/-143.40$ (m; F_{ortho} C_6F_5) , $-113.74/-113.80$ (s; F_{ortho} $C_6Cl_2F_3$), $-113.65/-115.42$ (s; F_{para} $C_6Cl_2F_3$); MS: *m*/*z* (%): 450 (1), 449 (2), 448 (9), 447 (3) $[M]^+$, 446 (13), 252 (52), 213 (35), 202 (33), 194 (43), 182 (100), 181 (70), 143 (26), 82 (28), 57 (33), 54 (26), 51 (38), 41 (55).

Compound 7: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.82$ (s, 1H; H^1), 4.62 (s, 1H; $H^{1'}$), 3.37 (s, 2H; H^3, $H^{3'}$), 1.75 (s, 3H; Me^2); ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -116.22$ (s; F_{ortho} $C_6Cl_2F_3$), -114.50 (s; F_{para} $C_6Cl_2F_3$); MS: *m*/*z* (%): 256 (29), 255 (6), 254 (33) $[M]^+$, 213 (78), 199 (34), 169 (3), 143 (88), 117 (15), 69 (13), 51 (22), 41 (100).

General procedure for catalytic coupling of allylic halides and 1: Palladium complex **2** (0.0052 g, 0.006 mmol) and the additive (0.012 mmol) were placed into an NMR tube. Solvent (0.5 mL), the allylic halide (0.240 mmol), and $Bu_3SnC_6Cl_2F_3$ (**1**) (0.240 mmol) were added, and the mixture was heated in an oil bath at 50 °C. The reactions were analyzed as described above.

Compound 3: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.83$ (m, 1H; H^2), 5.53 (d, $J = 10.2$ Hz, 1H; H^1), 3.82 (m, 1H; H^3), 2.12 (m, 2H; H^6, $H^{6'}$), 1.92 (m, 2H; H^4, H^5), 1.76 (m, 2H; $H^{4'}$, $H^{5'}$); ^{19}F NMR (282 MHz, $CDCl_3/CD_3CN$): $\delta = -115.35/-115.41$ (s; F_{ortho} $C_6Cl_2F_3$), $-115.19/-116.32$ (s; F_{para}, $C_6Cl_2F_3$); MS: *m*/*z* (%): 285 (2), 284 (13), 283 (9), 282 (61), 281 (13) $[M]^+$, 280 (100), 267 (42), 265 (67), 228 (49), 226 (75), 182 (86), 169 (27), 156 (17), 123 (7), 79 (12), 41 (23).

Compound 18: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.87$ (ddt, $J = 16.4$, 10.0, 6.3 Hz, 1H; H^2), 5.09 (dm, $J = 10.0$ Hz, 1H; H^1), 5.07 (dm, $J = 16.4$ Hz, 1H; $H^{1'}$), 3.42 (dqu, $J = 6.3$, 1.5 Hz, J(H-F) = 1.5 Hz, 2H; H^3, $H^{3'}$); ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -117.05$ (s; F_{ortho} $C_6Cl_2F_3$), -114.80 (s; F_{para} $C_6Cl_2F_3$); MS: *m*/*z* (%): 243 (2), 242 (14), 241 (5) $[M]^+$, 240 (33), 215 (20), 213 (20), 170 (54), 169 (100), 123 (24), 93 (30), 74 (41), 51 (39), 41 (23).

Synthesis of $[Pd(5\text{-}C_6F_5\text{-}\eta^3\text{-cyclohexenyl})(NCMe)_2]BF_4$ (11): Compound **2** (0.1510 g, 0.174 mmol) was added to a solution of $AgBF_4$ (0.0680 g, 0.349 mmol) in CH_3CN (30 mL). The mixture was protected from light and stirred for 30 min The solution was filtered and evaporated to about 0.5 mL. Et_2O (20 mL) was added to the residue, and the mixture was stirred in a cold bath for 30 min. A white solid was obtained that was filtered, washed with Et_2O, and dried under vacuum in a dessicator with P_2O_5 (0.131 g, 72% yield). ^{1}H NMR (300 MHz, CD_3CN): $\delta = 5.78$ (t, $J = 6.7$ Hz, 1H; H^2), 5.54 (t, $J = 6.7$ Hz, 2H; H^1, H^3), 2.78 (tt, $J = 12.0$, 6.0 Hz, 1H; H^5), 2.28 (m, $J = 18.0$, 6.0 Hz, 2H; H^4, H^6), 2.02 (m, $J = 18.0$, 12.0 Hz, 2H; $H^{4'}$, $H^{6'}$); ^{19}F NMR (282 MHz, CD_3CN): $\delta = -163.81$ (m; F_{meta}), -158.08 (t; F_{para}), -151.02 (m; BF_4), -142.32 (m; F_{ortho}); IR (Nujol,): $\tilde{\nu} = 2316\,cm^{-1}$ (m), $2287\,cm^{-1}$ (m); elemental analysis calcd (%) for $C_{16}H_{14}BF_9N_2Pd$ (522.5): C 36.77, H 2.70, N 5.30; found C 36.30, H 2.77, N 5.27.

Synthesis of $(NBu_4)[Ag(C_6Cl_2F_3)_2]$: $LiC_6Cl_2F_3$ was prepared at -80 °C by dropwise addition of BuLi (13.44 mmol in 30 mL of Et_2O) to a solution of $C_6Cl_3F_3$ (2.8690 g, 12.221 mmol) in Et_2O (30 mL). After 15 min $Ag(CF_3COO)$ (0.9 g, 4.074 mmol) was added and the mixture was stirred at low temperature and protected from light for 20 min. $(NBu_4)(CF_3COO)$ (1.7774 g, 5.000 mmol) was added, and the reaction mixture was stirred for 2 h, while the temperature slowly increased. After this time the suspension was evaporated to dryness and the residue was washed with

water twice. Then it was extracted with CH_2Cl_2 (3×15 mL) and filtered through $MgSO_4$ and activated charcoal. The filtrate was evaporated to a about 5 mL, and Et_2O (30 mL) was added. The resulting solution was cooled down and a white solid crystallized, which was filtered, washed with cold Et_2O (2×5 mL), and air dried (2 g, 65% yield). It should be stored protected from light. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.04$ (m, 8H; NCH_2 Bu), 1.51 (m, 8H; CH_2 Bu), 1.35 (m, $J = 7.0$ Hz, 8H; CH_2 Bu), 0.95 (t, $J = 7.0$ Hz, 12H; CH_3 Bu); ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -118.79$ (s, 2F; F_{para}), -82.5 (br s, 4F; F_{ortho}); elemental analysis calcd (%) for $C_{28}H_{36}AgCl_4F_6N$ (750.2): C 44.81, H 4.83, N 1.86; found C 44.95, H 4.73, N 1.85.

Synthesis of (NBu_4)[Pd(5-C_6F_5-η^3-cyclohexenyl) ($C_6Cl_2F_3$)$_2$] (12): $[Ag(C_6Cl_2F_3)_2](NBu_4)$ (0.1730 g, 0.231 mmol) was added to solution of **2** (0.1000 g, 0.115 mmol) in CH_2Cl_2 (20 mL). The mixture was protected from light and stirred for 30 min. The resulting suspension was filtered and evaporated to dryness. The residue was triturated with *n*-hexane (5 mL), and the mixture was cooled down. The white solid **12** was filtered, washed with hexane, and air-dried (0.2020 g, 88% yield). ^{1}H NMR (300 MHz, $CDCl_3/CD_3CN$): $\delta = 5.35/5.25$ (t, $J = 6.8$ Hz, 1H; H^2), 4.76/4.70 (t, $J = 6.8$ Hz, 2H; H^1, H^3), 2.92/3.04 (m, 8H; NCH_2 Bu), 2.70/2.66 (m, 1H; H^5), 2.47/2.43 (m, 2H; H^4, H^6), 2.15/2.16 (m, 2H; $H^{4'}$, $H^{6'}$), 1.50/1.57 (m, 8H; CH_2 Bu), 1.31/1.33 (m, 8H; CH_2 Bu), 0.92/0.95 (t, $J = 7.0$ Hz, 12H; CH_3 Bu); ^{19}F NMR (282 MHz, $CDCl_3/CD_3CN$): $\delta = -163.80/-164.41$ (m; F_{meta} C_6F_5), $-159.30/-160.00$ (t; F_{para} C_6F_5), $-141.58/-142.41$ (m; F_{ortho} C_6F_5), $-123.70/-124.00$ (s; F_{para} $C_6Cl_2F_3$), $-84.41/-84.98$ (s; F_{ortho} $C_6Cl_2F_3$); elemental analysis calcd (%) for $C_{40}H_{44}Cl_4F_{11}NPd$ (996.0): C 48.23, H 4.45, N 1.40; found C 47.47, H 4.39, N 1.54.

Synthesis of [$Pd_2(\mu$-$C_6Cl_2F_3)_2$(5-C_6F_5-η^3-cyclo hexenyl)$_2$] (13): Compound **2** (0.0653 g, 0.075 mmol) was added to a solution of $AgBF_4$ (0.0293 g, 0.151 mmol) in acetone (15 mL). The mixture was protected from light, stirred for 15 min, and then filtered. Complex **12** (0.1500 g, 0.151 mmol) was added to the filtrate and an orange solution was obtained immediately. After 30 min stirring the solution was evaporated to dryness, and EtOH was added (15 mL). The orange solid was filtered, washed with cold EtOH (2×5 mL), and air-dried (0.1230 g, 74% yield). When **13** is dissolved in acetonitrile a colorless solution of [(5-C_6F_5-η^3-cyclohexenyl)Pd($C_6Cl_2F_3$)(NCMe)] (**10**) was obtained.

Compound 13: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.60$, 5.50 (t, t, $J = 6.6$ Hz, 1H, 1H; $H^{2(cis+trans)}$), 4.76, 4.74 (t, t, $J = 6.6$ Hz, 2H, 2H; H^1, $H^{3(cis+trans)}$), 2.62 (m, 2H; $H^{5(cis+trans)}$), 2.20–1.80 (m, 8H; H^4, $H^{4'}$, H^6, $H^{6'(cis+trans)}$); ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -162.20$ (m, 4F; $F_{meta(cis+trans)}$ C_6F_5), -156.70, -156.60 (t, t, 1F, 1F; $F_{para(cis+trans)}$ C_6F_5), -141.70 (m, 4F; $F_{ortho(cis+trans)}$ C_6F_5), -108.82, -108.80 (s, s, 1F, 1F; $F_{para(cis+trans)}$ $C_6Cl_2F_3$), -74.85 (m, 1F; $F_{ortho,cis}$ $C_6Cl_2F_3$), -74.65 (m, 2F; $F_{ortho,trans}$ $C_6Cl_2F_3$), -74.15 (m, 1F; $F_{ortho,cis}$ $C_6Cl_2F_3$); elemental analysis calcd (%) for $C_{36}H_{16}Cl_4F_{16}Pd_2$ (1107.2): C 39.06, H 1.46; found C 38.94, H 1.60.

Compound 10: ^{1}H NMR (300 MHz, CD_3CN): $\delta = 5.57$ (t, $J = 6.6$ Hz, 1H; H^2), 5.50 (t, $J = 6.6$ Hz, 1H; H^1), 4.74 (m, 1H; H^3), 2.70 (m, 1H; H^5), 2.44 (m, $J = 17.5$, 5.0 Hz, 1H; H^6), 2.32 (m, $J = 17.5$, 11.0 Hz, 1H; $H^{6'}$), 2.06 (m, 2H; H^4, $H^{4'}$); H^1, *trans* to Rf; H^3, *trans* to NCMe; ^{19}F NMR (282 MHz, CD_3CN): $\delta = -164.39$ (m; F_{meta} C_6F_5), -159.10 (t; F_{para} C_6F_5), -142.41 (m; F_{ortho} C_6F_5), -121.35 (s; F_{para} $C_6Cl_2F_3$), -86.79 (m; F_{ortho} $C_6Cl_2F_3$).

Detection of intermediate [Pd(5-C_6F_5-η^3-cyclohexenyl) ($C_6Cl_2F_3$)-(*p*-benzoquinone)] (15): $CDCl_3$ (0.6 mL) was added to an NMR tube that contained **13** (0.005 g, 0.0045 mmol) and *p*-benzoquinone (0.001 g, 0.009 mmol) at 243 K. The reaction was monitored at this temperature by ^{19}F NMR and the formation of complex **15** was observed.

Complex **13** (0.0150 g, 0.013 mmol) was dissolved in a mixture of CH_2Cl_2 (2 mL) and CH_3CN (0.5 mL), and stirred at 0 °C until the solution became colorless and complex **10** was formed. The solution was then cooled at -50 °C and *p*-benzoquinone (0.0033 g, 0.03 mmol) was added; the mixture was evaporated to dryness at low temperature (below -30 °C). The residue was dissolved in $CDCl_3$ at 233 K and checked by NMR. The sample contained complex **15**, along with **13** and **10**.

Compound 15: ^{1}H NMR (300 MHz, $CDCl_3$, 233 K): $\delta = 6.52$, 6.46 (AB system, $J = 9.0$ Hz, 2H; *p*-benzoquinone), 6.08 (t, $J = 6.2$ Hz, 1H; H^1), 6.01 (t, $J = 6.2$ Hz, 1H; H^3), 5.52 (t, $J = 6.2$ Hz, 1H; H^2), 5.47, 5.43 (AB system, $J = 9.0$ Hz, 2H; *p*-benzoquinone), 2.88 (m, 1H; H^5), 2.8–1.8 (4H; H^4, $H^{4'}$, H^6, $H^{6'}$); ^{19}F NMR (282 MHz, $CDCl_3$, 243 K): $\delta = -160.98$ (m; F_{meta} C_6F_5), -154.95 (t; F_{para} C_6F_5), -141.57 (m; F_{ortho} C_6F_5), -116.49 (s; F_{para} $C_6Cl_2F_3$), -92.39 (br s; F_{ortho} $C_6Cl_2F_3$), -89.80 (s; F_{ortho} $C_6Cl_2F_3$).

X-ray crystal structure determination: Crystals of **13** were obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of the complex at -20 °C. An orange prism of dimensions $0.2 \times 0.07 \times 0.02$ mm was mounted on the tip of a glass fiber. X-ray measurements were made using a Bruker SMART CCD area-detector diffractometer with Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å).

Crystal data: triclinic $P\bar{1}$: $a = 7.9171(10)$, $b = 9.7405(12)$, $c = 12.6192(15)$ Å; $\alpha = 77.172(2)^\circ$, $\beta = 82.665(2)^\circ$, $\gamma = 74.696(3)^\circ$; $V = 912.74(19)$ Å^3; formula unit: $C_{36}H_{16}Cl_4F_{16}Pd_2$ with $Z = 1$; formula weight = 1107.09; calculated density = 2.014 g cm^{-3}; $F(000) = 536$; $\mu(Mo_{K\alpha}) = 1.389$ mm^{-1}. 4299 reflections were collected ($1.66^\circ > \theta > 23.29^\circ$). Intensities were integrated and the structure was solved by direct methods procedure.[34] Full-matrix least-squares refinement (on F^2) based on 2619 independent reflections converged with 262 variable parameters and no restraints. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. $R1 = 0.0403$, for $F^2 > 2\sigma(F^2)$; $wR2 = 0.0772$.[35] GoF (F^2) = 0.900. $\Delta\rho_{max} = 0.704$, $\Delta\rho_{min} = -0.508$ e Å^3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-152686. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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