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The influence of the nature of phosphine ligand on palladium catalysts for cross-coupling of weakly nucleophilic potassium pentafluorophenyltrifluoroborate with ArHal and $PhCH_2Hal$ (Hal=Br, Cl)

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ABSTRACT

The influence of the ligand nature on catalytic activity of palladium catalysts for cross-coupling of weakly nucleophilic potassium pentafluorophenyltrifluoroborate, which imitates the behavior of electron-deficient organoboron reagents, with aryl halides, ArHal (Hal=Br, Cl) was studied. The activity of the catalysts generated in situ from $Pd(OAc)_2$ and appropriate phosphorous containing ligands and the reaction selectivity was found to depend on the nature of bulky phosphines used as ligands. As a result, conditions for involving the electron-deficient organoboron reagent—potassium pentafluorophenyltrifluoroborate—in the palladium-catalyzed cross-coupling with aryl bromides and aryl chlorides were identified. It was demonstrated that the chosen conditions are appropriate for the reaction of $K[C_6F_5BF_3]$ with benzyl chloride and benzyl bromide deriving pentafluorophenylarylmethanes, $C_6F_5CH_2Ar$.

1. Introduction

Great progress has been made in Suzuki–Miyaura reactions in the last two decades. However, involving organoboron reagents $RB(OR')_2$ or $K[RBX_3]$ (X=F, OMe) with a strong electron-withdrawing moiety, R, in these processes remains a challenge because of the low reactivity and/or side-reactions under typical cross-coupling conditions.[1–6] From this standpoint, the known palladium-catalyzed interaction of polyfluorinated organoboron compounds with organic electrophiles (aryl halides, arenediazonium salts and aryl sulfonates) are an important transformation that imitates the behavior of electron-deficient and heteroaromatic organoboron reagents in cross-coupling reactions.[1–8] For example, 2-(polyfluorophenyl)pyridines were prepared by the reaction of 2,4,6-$C_6F_3H_2B(OH)_2$ or $C_6F_5B(OH)_2$ with 2-iodopyridine in the presence of $[Pd(PPh_3)_4]$, *t*-BuOK and Ag_2O in DME at 70–90 °C to give 32 and 76% yield, respectively.[9] The reaction of $C_6F_5B(OH)_2$ with 2-bromothiophene leads to the target product at 20% (in DME) or 68% (in DMF) yields only after substitution of K_3PO_4 for *t*-BuOK.[10] The found conditions were applicable for preparation of a series of 2-pentafluorophenyl- and 2,5-bis(pentafluorophenyl)thiophenes as well as the corresponding selenophene.[10] The cross-coupling of $C_6F_5B(OH)_2$ with aryl iodides and bromides catalyzed by $Pd_2(dba)_3/2P(t\text{-}Bu)_3$ gives 2,3,4,5,6-pentafluorobiphenyl ranging in 60–90% yields when performed in DME at 70 °C in the presence of CsF and Ag_2O.[11]

The promising alternative to polyfluoroorganoboronic acids are the corresponding polyfluoroorganoborates, $M[R_FBX_3]$ (X=OMe, F),[4–6,12] even though their use requires some adaptation of the conditions previously chosen for the non-fluorinated analogues. Thus, perfluorinated salt $K[C_6F_5BF_3]$ does not react with arenediazonium tetrafluoroborates under conditions suitable for cross-coupling for non-fluorinated salts $K[RBF_3]$ (R=aryl, alkenyl) ($Pd(OAc)_2$, dioxane, 20 °C).[13] Borates $K[C_6F_nH_{5-n}BF_3]$ (n=3–5) interact with $[4\text{-}XC_6H_4N_2][BF_4]$ to give polyfluorinated biphenyls (20–60% yields) in the presence of $[Pd(PPh_3)_4]$ instead of $Pd(OAc)_2$ (DME, 20 °C).[13] The reaction of cross-coupling of $K[C_6F_5BF_3]$ with less electrophilic aryl iodides 4-XC_6H_4I is observed in the presence of a catalyst generated in situ from $Pd(OAc)_2$ and $2PPh_3$[14] or $[Pd(PPh_3)_2Cl_2]$ and SIMes·HCl or IMes·HCl[15] in toluene at 100 °C in the presence of Ag_2O. A series of 2,3,4,5,6-pentafluorobiphenyl and 3,3′-bis(pentafluorophenyl)binaphthyl derivatives were prepared this way. Good results are usually obtained in cross-coupling of non-, mono- and difluorinated aryltrifluoroborates with aryl

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bromides. Alternatively, moderate yields (25–40%) of the desired products are observed in Pd-catalyzed polyfluoroarylation of ArBr with $K[C_6F_nH_{5-n}BF_3]$ (n=3–5) under identical conditions.[3,14,15]

In terms of the general problem, i.e., involving electron-deficient organotrifluoroborates in cross-coupling with carbon electrophiles, we studied the reaction of potassium pentafluorophenyltrifluoroborate, $K[C_6F_5BF_3]$ (**1**), with ArHal and $PhCH_2Hal$ (Hal=Br, Cl) using catalysts prepared from inexpensive $Pd(OAc)_2$ and a series of phosphine ligands of different nature.

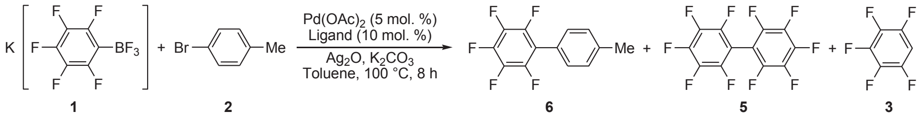
2. Results and discussion

2.1. Interaction of potassium pentafluorophenyltrifluoroborate (1) with 4-bromotoluene (2)

To achieve the optimal catalytic interaction of borate **1** with 4-bromotoluene (**2**) we used typical conditions of the cross-coupling reaction of borate **1** with aryl halides: 1.2 equiv of borate **1**, 1.2 equiv of Ag_2O, and 2 equiv of K_2CO_3 were added to 1 equiv of compound **2** introduced into the reaction mixture (Table 1).[1,2] K_2CO_3 is required to remove acidic admixtures that are produced during the reaction and lead to the formation of fluorinated borate $C_6F_5BF_2$, which is responsible for the formation of pentafluorobenzene (**3**) as a hydrodeboration product.[16,17]

Table 1

Cross-coupling of $K[C_6F_5BF_3]$ (**1**) with 4-bromotoluene (**2**) catalyzed by $Pd(OAc)_2$/2Ligand



Entry	Ligand	Conversion of **2**, %	Products, equiv (%)[a]			Selectivity toward **6**, %
			6	5	3	
1.	PPh_3	30	0.30 (25)[b]	Traces	0.07 (6)	100
2.	P(o-Tol)$_3$	87	0.87 (73)	n.o.	0.10 (8)	100
3.	XantPhos	98	0.68 (57)[c]	n.o.	0.07 (6)	70
4.	JohnPhos	69	0.62 (52)	0.02 (2)	0.19 (16)	90
5.	Cyclohexyl JohnPhos	44	0.34 (28)[d]	Traces	0.17 (14)	77
6.	MePhos	96	0.96 (80)	n.o.	0.05 (4)	100
7.	SPhos	94	0.93 (78)	0.01 (1)	0.06 (5)	99
8.	DavePhos	98	0.98 (82)	n.o.	0.07 (6)	100
9.	XPhos	100	1.00 (83)	Traces	0.02 (2)	100
10.	RuPhos	100	1.00 (83)	0.01 (1)	0.02 (2)	100
11.	1-Methyl-2-(2-dicyclohexylphosphinophenyl)-1*H*-benzoimidazole	80	0.68 (57)[e]	n.o.	0.07 (6)	85
12.	$P(Cy)_3$	100	1.00 (83)	n.o.	0.05 (4)	100
13.	P(t-Bu)$_3$	100	1.00 (83)	0.02 (2)	0.08 (7)	100

[a] Relative to **1**.
[b] 0.01(1) equiv of **4** were obtained.
[c] 0.19(16) equiv of **4** were obtained.
[d] 0.01(1) equiv of not identified product containing C_6F_5 group were obtained.
[e] 0.03(3) equiv of not identified product containing C_6F_5 group were obtained.

The active catalyst was prepared in situ from $Pd(OAc)_2$ and phosphorus containing ligands (see Fig. 1).[18–22] The data obtained by screening of the catalytic activity of different palladium complexes to the reaction of **1** with bromide **2** (Table 1) are presented in Table 1. The tabulated results show that the catalyst prepared from $Pd(OAc)_2$ and PPh_3 is comparatively less active (Table 1, entry 1), agreeing with the data obtained with a similar palladium catalyst system.[14] The catalytic activity of the palladium complexes increases considerably with the sterically hindered phosphines P(o-Tol)$_3$ or XantPhos but is as yet far from optimal (Table 1, entries 2 and 3). The formation of 2,3,4,5,6-pentafluorobiphenyl (**4**) was observed with PPh_3 (Table 1, entry 1) and XantPhos (Table 1, entry 3) but not with P(o-Tol)$_3$, confirming the tendency to quaternization for aromatic phosphines.[23]

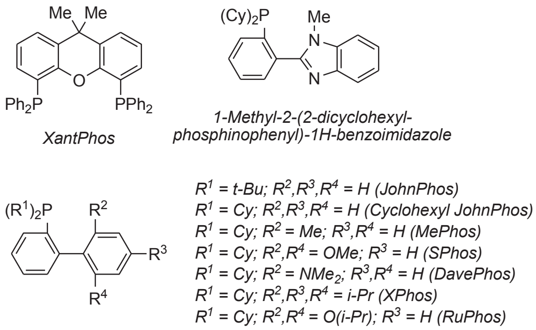


Fig. 1. Phosphorus containing ligands used for preparation of the palladium catalysts.

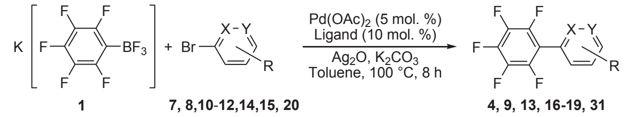
Earlier, Buchwald et al. offered a series of phosphine ligands with biaryl moieties to study a variety of the palladium-catalyzed cross-coupling reactions with aryl chlorides and bromides.[24,25] The effectiveness of these ligands was accounted for by a combination of specific electron and steric properties, which favor mainly the oxidative addition and reductive elimination steps of the catalytic cycle. A significant feature of the ligands is the existence of the phosphine-free aryl ring in the biaryl unit, which stabilizes the Pd(0) catalyst through favorable interactions with the π-system. The presence of substituents at the *ortho*-position of this ring prevents *ortho*-metalation and also provides the further increase in steric bulk.[26,27] Initial attempts to affect the cross-coupling of borate **1** with compound **2** using *JohnPhos* or *Cyclohexyl JohnPhos* failed in general (Table 1, entries 4 and 5) despite the successful utility of these ligands for the room-temperature Suzuki reactions of non-fluorinated arylboronic acids with aryl chlorides.[25] The use of *MePhos* as the ligand makes the catalyst more active (Table 1, entry 6) than the one observed before with *JohnPhos* and *Cyclohexyl JohnPhos*. Similar results were obtained with *SPhos* and *DavePhos* (Table 1, entries 7 and 8). Among the biphenyl bearing ligands, *XPhos* and *RuPhos* were found the best (Table 1, entries 9 and 10). In this case, cross-coupling of **1** with **2** was not complicated by side processes of the formation of biphenyl **5**, which is a formal product of oxidative coupling of borate **1**. The factors responsible for the appearance of perfluorobiphenyl (**5**) among the reaction products remain unclear in all of the above examples of cross-coupling of **1** with **2**.

Recently, 1-methyl-2-(2-dicyclohexylphosphinophenyl)-1*H*-benzoimidazole has been applied successfully for promoting the reactions of potassium phenyltrifluoroborate and aryl chlorides.[28] However, this ligand gives a less effective catalyst for coupling of **1** with **2** (Table 1, entry 11) than the ones tested in previous entries 6–10. The best results were obtained with the catalysts comprising Pd(OAc)$_2$ and P(*t*-Bu)$_3$ or P(Cy)$_3$ when the target biphenyl **6** was formed at a close to the quantitative selectivity (Table 1, entries 12 and 13).

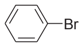
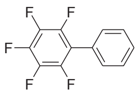
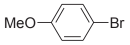
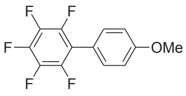
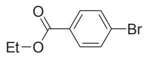
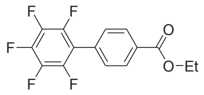
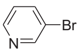
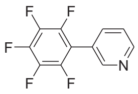
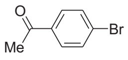
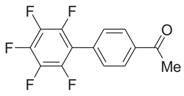
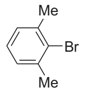
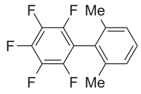
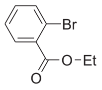
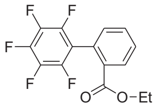
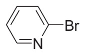
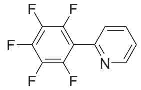
2.2. Interaction of potassium pentafluorophenyltrifluoroborate (1) with aryl bromides

The chosen reaction conditions were used for cross-coupling of **1** with electron-rich and electron-deficient aryl bromides (Table 2).

Table 2
Cross-coupling of K[C$_6$F$_5$BF$_3$] (**1**) with aryl bromides catalyzed by Pd(OAc)$_2$/2Ligand



X = CH; Y = CH; R = H, 4-OMe, 4-COMe, 4-COOEt, 2-COOEt, 2,6-Me$_2$
X = N; Y = CH; R = H
X = CH; Y = N; R = H

Entry	Aryl bromide	Ligand	Product	Yield, %
1.	 (**7**)	P(*t*-Bu)$_3$	 (**4**)	100
2.	**7**	P(Cy)$_3$	**4**	100
3.	 (**8**)	P(*t*-Bu)$_3$	 (**9**)	97
4.	**8**	P(Cy)$_3$	**9**	100
5.	 (**10**)	P(*t*-Bu)$_3$	 (**31**)	100
6.	**10**	P(Cy)$_3$	**31**	100
7.	 (**11**)	P(*t*-Bu)$_3$	 (**18**)	100
8.	**11**	P(Cy)$_3$	**18**	100
9.	 (**12**)	P(*t*-Bu)$_3$	 (**13**)	69
10.	**12**	P(Cy)$_3$	**13**	86
11.	**12**	XPhos	**13**	85
12.	 (**14**)	P(*t*-Bu)$_3$	 (**16**)	78
13.	 (**15**)	P(*t*-Bu)$_3$	 (**17**)	87
14.	**14**	XPhos	**16**	92
15.	**15**	XPhos	**17**	98
16.	**14**	P(Cy)$_3$	**16**	19
17.	**15**	P(Cy)$_3$	**17**	14
18.	 (**20**)	XPhos	 (**19**)	51
19.	**20**	P(*t*-Bu)$_3$	**19**	28
20.	**20**	P(Cy)$_3$	**19**	33

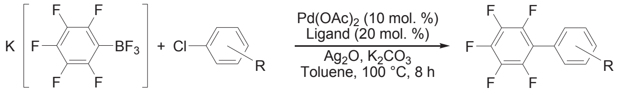
Similar to 4-bromotoluene, bromobenzene (**7**), and 4-bromoanisole (**8**) gave 2,3,4,5,6-pentafluorobiphenyl (**4**) and 2,3,4,5,6-pentafluoro-4′-methoxybiphenyl (**9**), respectively, at high yields using both P(*t*-Bu)$_3$ and P(Cy)$_3$ ligands (Table 2, entries 1–4). These ligands also were highly effective in cross-coupling of **1** with ethyl 4-bromobenzoate (**10**) and 3-bromopyridine (**11**) bearing electron-deficient aryl group (Table 2, entries 5–8). The reaction with 4-bromoacetophenone (**12**) promoted by a catalyst prepared from Pd(OAc)$_2$ and P(*t*-Bu)$_3$ gave 2,3,4,5,6-pentafluoro-4′-acetylbiphenyl (**13**) in 69% yield (Table 2, entry 9) while the yield of **13** increased to 85–86% with P(Cy)$_3$ or XPhos as ligands (Table 2, entries 10 and 11).

In moving to sterically hindered aryl bromides, we discovered that the result were independent of the electron nature of substituent X in *ortho*-position to the bromine atom. Thus, the reactions of K[C$_6$F$_5$BF$_3$] with 2,6-dimethylbromobenzene (**14**) and ethyl 2-bromobenzoate (**15**) gave, as expected, 2,3,4,5,6-pentafluoro-2′,6′-dimethylbiphenyl (**16**) and 2,3,4,5,6-pentafluoro-2′-ethoxycarbonylbiphenyl (**17**), respectively, in the presence of Pd(OAc)$_2$/2P(*t*-Bu)$_3$ or 2XPhos as catalysts (Table 2, entries 12–15), whereas the reactions were slow and less effective (the product yields were no more than 20%) when catalyzed by Pd(OAc)$_2$/2P(Cy)$_3$ (Table 2, entries 16 and 17). The observed activity of the catalysts prepared using P(*t*-Bu)$_3$, P(Cy)$_3$, and XPhos may be accounted for by a decrease in their cone angles from 256° for *XPhos* to 170° for P(Cy)$_3$ through 182° for P(*t*-Bu)$_3$.[29] While an excellent yield of 3-(pentafluorophenyl)pyridine (**18**) was observed (Table 2, entries 7 and 8), it was reasonable to expect a high yield of its isomeric 2-(pentafluorophenyl)pyridine (**19**) derived from 2-bromopyridine (**20**), but that was not the case. A moderate yield of product **19** was only obtained using ligand XPhos (Table 2, entry 18) whereas both phosphines P(*t*-Bu)$_3$ and P(Cy)$_3$ were less effective (Table 2, entries 19 and 20). It seems like the nitrogen atom stabilizes the reactive intermediate formed in the catalytic cycle to cause eventually the catalyst deactivation.

2.3. Interaction of potassium pentafluorophenyltrifluoroborate (1) with aryl chlorides

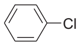
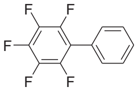
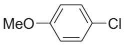
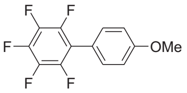
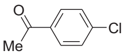
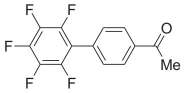
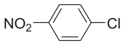
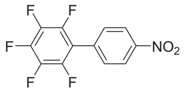
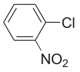
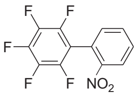
In general, the reaction is slower with aryl chlorides than with aryl bromides and iodides. However, the use of 10 mol % of Pd(OAc)$_2$ and 20 mol % of phosphine ligand provides acceptable results over a period of 8 h (Table 3).

Table 3
Cross-coupling of K[C$_6$F$_5$BF$_3$] (**1**) with aryl chlorides catalyzed by Pd(OAc)$_2$/2Ligand



1 **21-24**, **26** **4**, **9**, **13**, **25**, **27**

R = H, 4-OMe, 4-COMe, 2-NO$_2$, 4-NO$_2$

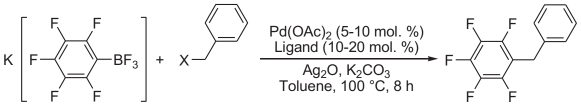
Entry	Substrate	Ligand	Product	Yield, %
1.	 (**21**)	XPhos	 (**4**)	67
2.	 (**22**)	XPhos	 (**9**)	50
3.	**21**	P(*t*-Bu)$_3$	**4**	27
4.	**21**	P(Cy)$_3$	**4**	8
5.	**22**	P(*t*-Bu)$_3$	**9**	24
6.	**22**	P(Cy)$_3$	**9**	4
7.	 (**23**)	P(*t*-Bu)$_3$	 (**13**)	36
8.	**23**	P(Cy)$_3$	**13**	74
9.	**23**	XPhos	**13**	40
10.	 (**24**)	P(*t*-Bu)$_3$	 (**25**)	76
11.	**24**	P(Cy)$_3$	**25**	29
12.	**24**	XPhos	**25**	90
13.	 (**26**)	P(*t*-Bu)$_3$	 (**27**)	23
14.	**26**	XPhos	**27**	55

Cross-coupling of **1** with chlorobenzene (**21**) and 4-methoxy chlorobenzene (**22**) catalyzed by Pd(OAc)$_2$/2XPhos produced corresponding biphenyls **4** and 2,3,4,5,6-pentafluoro-4′-methoxybiphenyl (**9**) (67 and 50% yield, respectively, see Table 3, entries 1 and 2). Substitution of P(*t*-Bu)$_3$ and P(Cy)$_3$ for XPhos led to unsatisfactory results (Table 3, entries 3-6). Pentafluorophenylation of more reactive 4-chloroacetophenone (**23**) and 4-nitrochloro benzene (**24**) containing a highly electron-deficient substituent was much faster to produce products **13** and 2,3,4,5,6-pentafluoro-4′-nitrobiphenyl (**25**) (74–90 % yields, see Table 3, entries 7–12). Obviously, the role of the steric factor for aryl chlorides becomes more significant than in the case of the cross-coupling of aryl bromides. The reaction of **1** with 2-nitrochlorobenzene (**26**) catalyzed by either P(*t*-Bu)$_3$ or XPhos resulted in lower yields of 2,3,4,5,6-pentafluoro-2′-nitrobiphenyl (**27**) (Table 3, entries 13 and 14) than the yields of biphenyl **25** obtained with the same phosphines.

2.4. Interaction of potassium pentafluorophenyltrifluoroborate (1) with benzyl halides

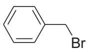
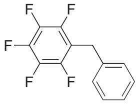
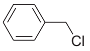
Recently it has been demonstrated that cross-coupling of arylboronic acids or potassium aryltrifluoroborates with benzyl halides is one of the most convenient ways to diarylmethanes,[30–34] which are observed in supramolecular structures and biologically active compounds.[35–38] Their tetra- and pentafluorinated analogues can be synthesized by benzylation of corresponding polyfluorobenzenes,[39,40] pentafluorobenzoyl chloride,[41] bromopentafluorobenzene[42] or by the reaction between arylboronic acids and pentafluorobenzyl bromide.[43,44] Our studies demonstrated that the suggested system is appropriate for cross-coupling of borate **1** with benzyl bromide (**28**) and benzyl chloride (**29**) too (Table 4). Although these are preliminary results that need further optimization, desired 1-benzyl-2,3,4,5,6-pentafluorobenzene (**30**) was obtained with moderate yields using Pd(OAc)$_2$ and P(Cy)$_3$ or XPhos (Table 4, entries 2, 3). The effect of bulky phosphine P(*t*-Bu)$_3$ is as yet not clearly understood. When it was used for cross-coupling, the yield of **30** was lower with than P(Cy)$_3$ or XPhos (Table 4, entry 1) but noticeably higher with less reactive PhCH$_2$Cl (Table 4, entry 4). The studies in the field are in progress.

Table 4
Cross-coupling of K[C$_6$F$_5$BF$_3$] (**1**) with benzyl bromide (**28**) and benzyl chloride (**29**) catalyzed by Pd(OAc)$_2$/2Ligand



1 **28**, **29** **30**

X = Br, Cl

Entry	Substrate	Ligand	Product	Yield, %
1.	 (**28**)	P(*t*-Bu)$_3$	 (**30**)	23
2.	**28**	P(Cy)$_3$	**30**	46
3.	**28**	XPhos	**30**	47
4.	 (**29**)	P(*t*-Bu)$_3$	**30**	38

3. Conclusion

Palladium complexes formed in situ from $Pd(OAc)_2$ and bulky phosphines XPhos, $P(t\text{-}Bu)_3$, and $P(Cy)_3$ are effective catalysts for cross-coupling of weakly nucleophilic potassium pentafluorophenyltrifluoroborate with both aryl bromides and aryl chlorides. The catalyst activity as well as the reaction selectivity, especially in the case of a sterically hindered substrate, appears to be determined by the nature of the phosphine ligands. Thus, catalytic systems derived from $Pd(OAc)_2$ and $P(t\text{-}Bu)_3$ or XPhos operate successfully for *ortho*-substituted aryl bromides and aryl chlorides. The found conditions are applicable for involving of **1** in cross-coupling with benzyl bromide and benzyl chloride, which is a new approach to synthesis of 2,3,4,5,6-pentafluorodiarylmethanes, $C_6F_5CH_2Ar$.

4. Experimental part

4.1. General

The NMR spectra were acquired using a Bruker AVANCE 300 (^{19}F 282.40 MHz) and Bruker DRX 500 (^{1}H 500.13 MHz; ^{13}C 125.76 MHz) spectrometers. The chemical shifts are assigned to TMS (^{1}H, ^{13}C), CCl_3F (^{19}F, with C_6F_6 as secondary reference (−162.9 ppm)). GC–MS analysis was performed using a Shimadzu GCMS-QP2010 Plus (with GsBP-1MS column) instrument. GC analysis was carried out using a Chromos GC-1000 equipped with a capillary column (SGE, ID-BP1, 0.25 μm×0.32 mm×25 m). High resolution mass spectra were acquired using an AMD 604 spectrometer (EI mode, 70 eV). Palladium acetate (Fluka), silver oxide (Degussa), PPh_3 (Panreac), $P(o\text{-}Tol)_3$ (Fluka), $P(t\text{-}Bu)_3$ (Aldrich), $P(Cy)_3$ (Acros), MePhos (Acros), Cyclohexyl JohnPhos (Acros), XPhos (Acros), SPhos (Acros), DavePhos (Acros), RuPhos (Acros), XantPhos (Acros), JohnPhos (Aldrich), 1-methyl-2-(2-dicyclohexylphosphinophenyl)-1*H*-benzoimidazole (PCy PhMezole-phos, Aldrich), aryl halides (Acros), benzyl chloride (Acros), and benzyl bromide (Fluka) were used as supplied. Potassium pentafluorophenyltrifluoroborate (**1**) was prepared as described elsewhere.[15] K_2CO_3 was calcinated at 450 °C and stored into a glovebox before being used. Solids were weighed inside a glovebox (less than 0.1 ppm O_2 and H_2O). Toluene was degassed using the freeze–pump–thaw method three times prior to the reaction. All reactions were carried out in a dry argon atmosphere.

Products 2,3,4,5,6-pentafluorobiphenyl (**4**),[45] 2,3,4,5,6-pentafluoro-4′-methylbiphenyl (**6**),[45] 2,3,4,5,6-pentafluoro-4′-methoxybiphenyl (**9**),[45] 2,3,4,5,6-pentafluoro-2′,6′-dimethylbiphenyl (**16**),[45] 2,3,4,5,6-pentafluoro-4′-ethoxycarbonylbiphenyl (**31**),[45] 3-(pentafluorophenyl)pyridine (**18**),[45] 2,3,4,5,6-pentafluoro-4′-acetylbiphenyl (**13**),[46] 2-(pentafluorophenyl)pyridine (**19**),[47] 1-benzyl-2,3,4,5,6-pentafluorobenzene (**30**),[43,48] 2,3,4,5,6-pentafluoro-2′-nitrobiphenyl (**27**),[49] and 2,3,4,5,6-pentafluoro-4′-nitrobiphenyl (**25**)[47] were authentic to earlier described compounds (^{1}H, ^{19}F, ^{13}C NMR spectra and the high resolution mass spectra). Yields were determined by ^{19}F NMR and gas chromatography using $C_6H_5CF_3$ as an internal quantitative standard.

4.2. The cross-coupling reaction of $K[C_6F_5BF_3]$ (1) with 4-bromotoluene (2) catalyzed by $Pd(OAc)_2$/2Ligand (optimization)

Palladium acetate (1.9 mg, 0.0084 mmol), phosphine ligand (0.0167 mmol), Ag_2O (46.4 mg, 0.2000 mmol), $K[C_6F_5BF_3]$ (54.8 mg, 0.2000 mmol), K_2CO_3 (46.2 mg, 0.3340 mmol), 4-bromotoluene (28.6 mg, 0.1670 mmol), and toluene (1.0 mL) were placed successively into a flask supplied with a magnetic stir bar. The reaction mixture was stirred at 100 °C (bath) for 8 h, cooled to 25 °C, charged with an internal standard $C_6H_5CF_3$ (10.0 μL, 0.0820 mmol) and analyzed by ^{19}F NMR and GC (Table 1).

4.3. The cross-coupling reaction of $K[C_6F_5BF_3]$ (1) with ethyl 2-bromobenzoate (15) catalyzed by $Pd(OAc)_2/2P(t\text{-}Bu)_3$ (general procedure)

$Pd(OAc)_2$ (1.9 mg, 0.0084 mmol), $P(t\text{-}Bu)_3$ (3.4 mg, 4.1 μL, 0.0167 mmol), Ag_2O (46.4 mg, 0.2000 mmol), $K[C_6F_5BF_3]$ (54.8 mg, 0.2000 mmol), K_2CO_3 (46.2 mg, 0.3340 mmol) were placed into a flask supplied with a magnetic stir bar. Then toluene (1.0 mL) and ethyl 2-bromobenzoate (38.3 mg, 27.0 μL, 0.1670 mmol) were added. The flask was placed into a bath (100 °C) and the reaction mixture was stirred for 8 h. The reaction mixture was cooled to 20 °C, charged with an internal standard $C_6H_5CF_3$ (10.0 μL, 0.0820 mmol) and analyzed by ^{19}F NMR The cross-coupling reaction of $K[C_6F_5BF_3]$ with other aryl bromides was performed the same way (Table 2).

To isolate previously unidentified biphenyl **17**, the reaction mixture was filtered through a silica gel plug (silica gel 60 μM). The filter was washed with toluene (2.0 mL) and the combined toluene solution was evaporated at reduced pressure to yield biphenyl **17** (44 mg, 83%).

*4.3.1. 2,3,4,5,6-Pentafluoro-2′-ethoxycarbonyl-biphenyl (**17**).* ^{19}F NMR ($CDCl_3$) −143.0 (dd, 2F, $^{3}J_{FF}$ 23.1 Hz, $^{5}J_{FF}$ 8.0 Hz, F-2,6), −157.0 (t, 1F, $^{3}J_{FF}$ 20.9 Hz, F-4), −164.3 (ddd, 2F, $^{3}J_{FF}$ 22.1, 21.9 Hz, $^{5}J_{FF}$ 7.2 Hz, F-3,5). ^{1}H NMR ($CDCl_3$) 8.17 (dd, $^{3}J_{HH}$ 7.8 Hz, $^{4}J_{HH}$ 1.1 Hz, 1H), 7.65 (ddd, $^{3}J_{HH}$ 7.6 Hz, $^{4}J_{HH}$ 1.1 Hz, 1H), 7.57 (ddd, $^{3}J_{HH}$ 7.7 Hz, $^{4}J_{HH}$ 1.0 Hz, 1H), 7.33 (d, $^{3}J_{HH}$ 7.7 Hz, 1H), 4.24 (q, $^{3}J_{HH}$ 7.1 Hz, 2H), 1.25 (t, $^{1}J_{HH}$ 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$) 165.5 (s, 1C, COO), 143.7 (dddd, 2C, $^{1}J_{CF}$ 246 Hz, $^{2}J_{CF}$ 15 Hz, $^{3}J_{CF}$ 7 Hz, $^{4}J_{CF}$ 4 Hz, C-2,6), 140.3 (dtt, 1C, $^{1}J_{CF}$ 253 Hz, $^{2}J_{CF}$ 13 Hz, $^{3}J_{CF}$ 5 Hz, C-4), 137.2 (ddddd, 2C, $^{1}J_{CF}$ 250 Hz, $^{2}J_{CF}$ 17, 13 Hz, $^{3}J_{CF}$ 5 Hz, $^{4}J_{CF}$ 2 Hz, C-3,5), 132.1 (s, 1C, C-5′), 131.7 (s, 1C, C-3′), 131.0 (s, 1C, C-6′), 130.3 (s, 1C, C-2′), 129.4 (s, 1C, C-4′), 126.9 (s, 1C, C-1′), 115.7 (td, 1C, $^{2}J_{CF}$ 19 Hz, $^{4}J_{CF}$ 4 Hz, C-1), 61.0 (s, 1C, CH_2O), 13.7 (s, 1C, CH_3). HRMS calcd for $C_{15}H_9F_5O_2$: 316.0523; found: 316.0524.

4.4. The cross-coupling reaction of $K[C_6F_5BF_3]$ (1) with 4-nitrochlorobenzene (24) catalyzed by $Pd(OAc)_2$/2Ligand (general procedure)

$Pd(OAc)_2$ (3.8 mg, 0.0167 mmol), XPhos (15.9 mg, 0.0334 mmol), 4-nitrochlorobenzene (26.3 mg, 0.1670 mmol), Ag_2O (46.4 mg, 0.2000 mmol), $K[C_6F_5BF_3]$ (54.8 mg, 0.2000 mmol), K_2CO_3 (46.2 mg, 0.3340 mmol) were placed into a flask supplied with a magnetic stir bar and toluene (1.0 mL) was added. The flask was placed into a bath (100 °C) and the reaction mixture was stirred for 8 h. The reaction mixture was cooled to 20 °C, charged with an internal standard $C_6H_5CF_3$ (10.0 μL, 0.0820 mmol) and analyzed by ^{19}F NMR. The cross-coupling reaction of $K[C_6F_5BF_3]$ with other aryl chlorides was performed the same way (Table 3).

4.5. The cross-coupling reaction of $K[C_6F_5BF_3]$ with benzyl halides 28 and 29 catalyzed by $Pd(OAc)_2$/2Ligand

A flask equipped with a magnetic stir bar was charged with $Pd(OAc)_2$ (1.9 mg, 0.0084 mmol), $P(t\text{-}Bu)_3$ (3.4 mg, 4.1 μL, 0.0167 mmol) (or the corresponding amount of $P(Cy)_3$ and XPhos), benzyl bromide (28.6 mg, 19.9 μL, 0.1670 mmol), Ag_2O (46.4 mg, 0.2000 mmol), $K[C_6F_5BF_3]$ (54.8 mg, 0.2000 mmol), K_2CO_3 (46.2 mg, 0.3340 mmol), and toluene (1.0 mL). The flask was placed into a bath (100 °C) and the reaction mixture was stirred for 8 h. The reaction mixture was cooled to 20 °C, charged with an internal standard $C_6H_5CF_3$ (10.0 μL, 0.0820 mmol) and analyzed by ^{19}F NMR. Reaction of **1** (54.8 mg, 0.2000 mmol) with benzyl chloride

(21.1 mg, 19.2 μL, 0.1670 mmol) was performed by analogy using $Pd(OAc)_2$ (3.8 mg, 0.0167 mmol), $P(t\text{-}Bu)_3$ (6.8 mg, 8.2 μL, 0.0334 mmol), Ag_2O (46.4 mg, 0.2000 mmol), K_2CO_3 (46.2 mg, 0.3340 mmol) and toluene (1.0 mL) (Table 4).

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.04.019.

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