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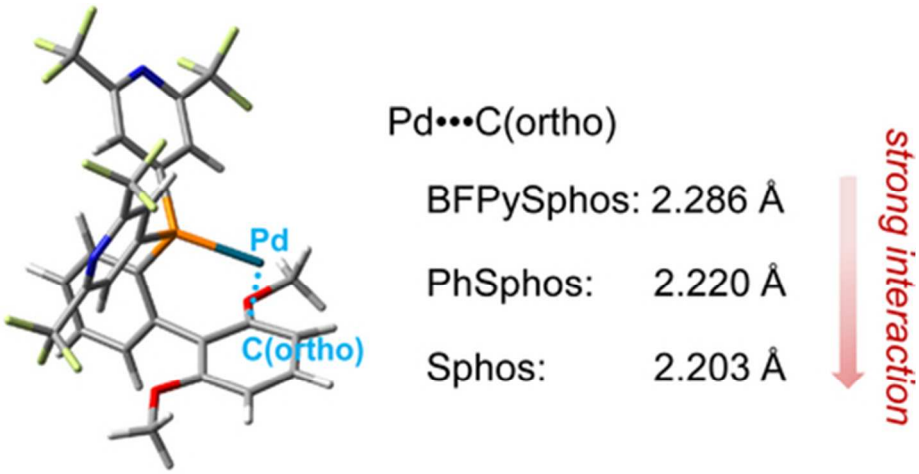

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ARTICLE

Highly Electron-poor Buchwald-type Ligand: Application for Pd-catalysed Direct Arylation of Thiophene Derivatives and Theoretical Consideration of the Secondary Pd^0-arene Interaction

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Highly electron-poor SPhos ligands bearing either 2,6-bis(trifluoromethyl)-4-pyridyl (BFPy) or 3,5-$(CF_3)_2C_6H_3$ groups were synthesised. The former ligand highly accelerated the Pd-catalysed direct arylation of 2-propylthiophene, 2-methylthiophene or benzo[*b*]thiophene with only 1 mol% of the catalyst. This high catalytic activity can be attributed to a combination of electronic properties and the secondary Pd–arene interaction of BFPySPhos. The secondary interactions of SPhos, PhSPhos and BFPySPhos were optimised at the oniom(mp2/lanl2dz:b3lyp/lanl2dz) level and were further evaluated using the NBO method by DFT at the M06-2X/6-31G(d) level with LandL2DZ + ECP. The deletion energy analysis showed that the transfer of electrons from Pd to aromatic ring is the dominating factor for the secondary Pd–arene interaction of SPhos-Pd^0 complexes. Although an electron-poor BFPySPhos does not particularly favour this type of interaction, this interaction is still substantial enough to sufficiently stabilise the BFPySPhos-Pd complex.

Introduction

Tertiary phosphine ligands are one of the most commonly used supporting ligands due to the ability of phosphines to control the catalytic activity and stereoselectivity of a metal-ligand complex catalyst.[1] Although triphenylphosphine (PPh_3) and other electron-rich phosphines are the most commonly employed phosphine ligands, the use of an electron-poor phosphine ligand can also provide a good ligand acceleration effect for the metal-ligand complex catalyst in some cases.[2] Using this concept, we developed a novel, highly electron-deficient ligand with fluoro-functional groups as the achiral or chiral supporting ligand.[3] This ligand exhibited an excellent acceleration effect for certain catalytic C–C bond formation reactions.[4] Among our developed ligands, the highly electron-poor triarylphosphine with 2,6-bis(trifluoromethyl)-4-pyridyl (BFPy) groups {$P(BFPy)_3$} provides a better acceleration effect than commercially available highly electron-poor $P(C_6F_5)_3$.[3c] Furthermore, we recently reported that the $P(BFPy)_3$ ligand accelerated intramolecular direct arylation.[5] This acceleration effect was attributed to the high electron-poor nature of the $P(BFPy)_3$ ligand, which was validated by density functional theory (DFT) calculations using the natural bond orbital (NBO) method.[5] However, when intermolecular direct arylation was conducted using $P(BFPy)_3$, the catalytic activity of Pd was similar to a Pd/PPh_3 catalyst. In this case, a small amount of Pd-black was visually confirmed, which indicated that the $P(BFPy)_3$-Pd complex had decomposed. Therefore, we hypothesised that the active species of $P(BFPy)_3$-Pd^0 was partially decomposed due to the weak electron-donating ability of $P(BFPy)_3$. This decomposition occurred when an intermolecular reaction with a relatively low reaction rate was conducted in a highly polar solvent at a high reaction temperature. To overcome the critical weak coordination ability of the electron-poor phosphine, we focussed on Buchwald-type ligands such as the biaryl-phosphine unit.[6] The excellent Buchwald-type ligand system was a tremendous breakthrough for Pd-catalysed C-C coupling and C–N coupling reactions.[7] When the phosphorous atom of the Buchwald-type ligands coordinates with Pd^0, the lower aromatic ring of these ligands can also interact with Pd^0 (Fig. 1).[8] This secondary Pd–arene interaction stabilises the metal-ligand complex. Therefore, if the strong electron-withdrawing BFPy groups are introduced in Buchwald-type ligands, the Pd^0-(BFPy phosphine) species would be stable even in a highly polar solvent at a high reaction temperature. Herein, we synthesised a novel SPhos ligand bearing BFPy groups for Pd-catalysed intermolecular direct arylation. Furthermore, the stabilisation of the Pd^0 species through the secondary Pd–arene interaction was theoretically investigated since the electronic effects of phosphine on this interaction were unknown.

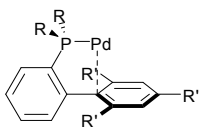

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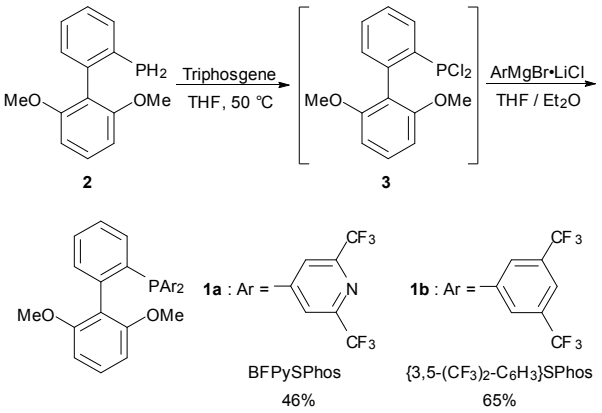
Fig. 1 Schematic view of the secondary Pd-arene Interaction of Buchwald-type ligand.

Results and discussion

Synthesis of highly electron-poor SPhos ligands

We first attempted to synthesise the SPhos[8c] ligand bearing BFPy groups (BFPySPhos, **1a**). Although many Buchwald-type biaryl-phosphine ligands have been reported,[6] the majority of ligands have Cy, Ph or other electron-donating groups on the phosphorous atom. In the synthesis of few Buchwald-type biaryl-phosphine ligands with fluoro-functionalised aryl groups (Ar^F) on the phosphorous atom,[9] an $(Ar^F)_2P$–Cl species had been used. Since $(BFPy)_2P$–Cl could not be obtained in its purified form, we chose to use phosphine **2**[10] as a synthetic intermediate (Scheme 1). The chlorination of **2** with triphosgene produced dichlorophosphine **3**. BFPyMgBr·LiCl was added to the reaction solution without any further purification of **3** to produce **1a** with a 45% yield. Novel ligand **1b**, which bears the 3,5-bis(tirfluoromethyl)phenyl groups, was also synthesised in a similar manner.



Scheme 1 Synthesis of BFPySPhos (**1a**) and {3,5-$(CF_3)_2$-C_6H_3}SPhos (**1b**).

Pd-catralysed direct arylation using 1a and 1b

Novel electron-poor SPhos ligands **1a** and **1b** were applied to direct arylation through a concerted metalation–deprotonation (CMD) process.[11] Since the catalyst for a direct arylation of Ar–H with Ar'–X exhibits a substrate specificity, it is necessary to find a suitable catalyst for the reaction of each substrate. The reactivity of the Ar–H component of the direct arylation reaction is usually the major determining factor.[12] For instance, 2-alkylthiophene or benzo[*b*]thiophene were less reactive substrates.[12,13] In the reactions using Pd/phosphine catalyst, Ozawa *et al*. have studied direct arylation of 2-methyl-thiophene.[14] Among them, the [Pd(2,6-$Me_2C_6H_3$)(OAc){P(2-$MeOC_6H_4)_3$}] catalyst was effective for the direct arylation of 2-methyl-thiophene with Ph–Br.[14d] The reaction was performed in the presence of 1 mol% of Pd catalyst at 100 °C for 12 h to produce an 89% yield of the coupled product. Meanwhile, Fagnou *et al*. reported that an electron-poor SPhos ligand bearing 4-CF_3–C_6H_4 groups accelerated the direct arylation of benzothiophene or 2-propylthiophene with Ar–I in the presence of a 5 mol% Pd catalyst at 100 °C for 16 h to produce coupled products with a 78% or 89% yield, respectively.[9b] In this study, we investigated the direct arylation of 2-propylthiophene to estimate the acceleration effect of the highly electron-poor SPhos **1**. The reactions of 2-propylthiophene with 4-CF_3–C_6H_4–Br were performed in the presence of 1 mol% $Pd(OAc)_2$/2 mol% phosphine ligand, which were either SPhos analogues or PR_3, with PivOH and K_2CO_3 in *N*,*N*-dimethylacetamide (DMA) at 100 °C for 3 h (Table 1). The extremely electron-poor **1a** was proven to be the most efficient ligand, and the **1a**-ligated Pd catalyst provided the desired product with a 90% yield (entry 1).

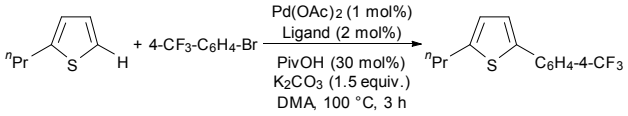


Table 1 Pd-catalyzed direct arylation of 2-propylthiophene[a]

Entry	Ligand	ν^{CO} (cm^{-1})[b]	Yield (%)[c]
1	BFPySPhos (**1a**)	2001	90
2	{3,5-$(CF_3)_2$-C_6H_3}SPhos (**1b**)	1991	62
3	(4-CF_3-C_6H_4)SPhos (**1c**)	1985	63
4	PhSPhos (**1d**)	1979	34
5	SPhos (**1e**)	1959	3
6	$P(BFPy)_3$ (**4a**)	2017	79
7	P{3,5-$(CF_3)_2$-C_6H_3}$_3$ (**4b**)	2000	75
8	P(4-CF_3-$C_6H_4)_3$ (**4c**)	1992	74
9	PPh_3 (**4d**)	1978	7
10	PCy_3 (**4e**)	1943	<1

[a] The reactions of 2-propylthiophene (0.39 mmol) with 4-bromobenzotrifluoride (0.32mmol) were performed in the presence of $Pd(OAc)_2$ (3.2 μmol) / ligand (6.4 μmol) with K_2CO_3 (0.48 mmol) and PivOH (0.096 mmol) at 100 °C for 3 h. [b] The ν^{CO} values of *trans*-[RhCl(phosphine)$_2$(CO)] in CH_2Cl_2. [c] Isolated yield.

Direct arylations of a few thiophene derivatives with aryl bromides were performed under the optimized conditions in the presence of $Pd(OAc)_2$/**1a** (Table 2). 4-Bromotoluene was relatively less reactive because electron-poor **1a** had a disadvantage for oxidative addition (entry 2). The direct arylation of 2-methylthiophene or benzo[*b*]thiophene, which were less reactive substrates,[12] also proceeded in the presence of $Pd(OAc)_2$/**1a** (entry 3, 4).

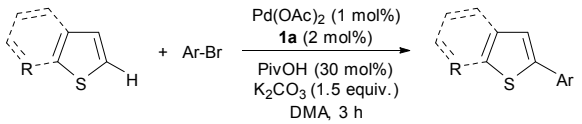
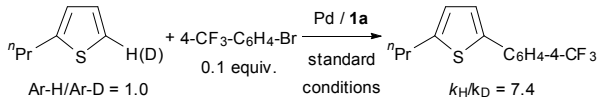


Table 2 Pd-catalysed direct arylation of thiophene derivatives[a]

Entry	Substrate	Ar	Temp. (°C)	Yield (%)[b]
1	2-propylthiophene	C_6H_5	100	89
2	2-propylthiophene	4-CH_3-C_6H_4	120	81
3	2-methylthiophene	4-CF_3-C_6H_4	100	90
4[c]	benzo[*b*]thiophene	4-CF_3-C_6H_4	95	87

[a] For 3 h. [b] Isolated yield. [c] For 5 h.

It has been previously reported that the electron-poor ligand accelerated either the CMD process[5] or the reductive elimination step[14c] in certain direct arylation reactions. To obtain the mechanistic information, the kinetic isotope effect was measured by comparing the initial rate for the direct arylation of 2-propylthiophene with 2-propylthiophene-*d* in competing experiments (Scheme 2). A pronounced kinetic isotope effect of 7.4 was obtained, which implies that the CMD process that involves a cleavage of the C–H bond was the rate determining step.



Scheme 2 The kinetic isotope effect of the direct arylation using Pd/**1a**.

In our previous theoretical studies of Pd-catalysed intramolecular direct arylation, the extremely electron-poor $P(BFPy)_3$ (**4a**) accelerated the CMD process by stabilising the Pd^{II}•••aromatic interaction to lower the energy levels of the CMD transition states.[5] In fact, the yields of the coupled product tend to increase with an increasingly electron-deficiency of the ligands, which were measured using the ν^{CO} values of *trans*-[RhCl(phosphine)$_2$(CO)] [3c,5,15] (Table 1). However, the more efficient ligand **1a** was more electron-rich than **4a**. Although Pd-black was never observed throughout the course of the reaction with **1a**, a trace amount of Pd-black was confirmed in the reaction with **4a**. Therefore, we hypothesised that the Pd/**1a** catalyst was seemingly more active than the Pd/**4a** catalyst due to the additional stabilisation from the secondary Pd–arene interactions in Pd/**1a**. In contrast, the Pd/**4a** catalyst partially decomposed during the catalytic reaction. We were thus prompted to theoretically examine the secondary Pd^0–arene interaction of the **1a**-Pd complex in greater detail.

Theoretical calculations of Pd-arene interaction

The secondary Pd^0–arene interaction in SPhos (**1e**) had been studied using X-ray crystallography[8b,8c] and computational chemistry.[8c,16] The X-ray crystal structure of **1e**-Pd(dba) (dba = dibenzylideneacetone) shows a η^1 Pd-C(ipso) interaction with a distance of 2.374(3) Å.[8c] Buchwald *et al*. optimised the complex at the B3LYP/3-21G* level to give a Pd-C(ipso) distance of 2.378 Å.[8c] In contrast, the **1e**-Pd complex without a dba ligand that is optimised using the B3LYP method with 6-31G/6-31G(d)/LANL2DZ + ECP gives a η^1 Pd–arene interaction with the *ortho* carbon {C(ortho)} as the lowest energy structure.[16a] To perform a unified analysis, we first re-estimated the **1e**-Pd(dba) complex using the DFT method (B3LYP or M06-2X) with 6-31G(d) for C, H, O and P and LandL2DZ + ECP for the Pd basis sets. These methods resulted in a significantly longer Pd-C(ipso) distance than the original calculated distance of 2.378 Å. When the complex was calculated at the oniom(mp2/lanl2dz:b3lyp/lanl2dz) level, whose high level layer is the atoms being related to the interaction with Pd, the Pd-C(ipso) distance of the resulting structure was 2.388 Å, which was similar to the distance obtained from X-ray crystallography. Therefore, we chose this particular calculation level for the optimisation of the **1a**-Pd complex.

To estimate the bond dissociation energies between Pd and phosphine, the **1**-Pd complexes with or without dba and the **4**-Pd complexes (R = **a**: BFPy, **d**: Ph, **e**: Cy) were calculated using the oniom method (Figure of Table 3). The resulting optimised structures of the **1**-Pd(dba) and **1**-Pd complexes were structurally similar to the reported Pd complexes of **1e** (Fig. 2). These are observed with a secondary Pd^0–arene interaction at C(ipso) in the **1**-Pd(dba) series and at C(ortho) in the **1**-Pd series. The bond dissociation energies (ΔH, ΔG) of **4**-Pd show that the extent of the Pd-phosphorous bonding is proportional to the electron-donating ability of **4** (Table 3). The ΔH and ΔG values in either the **1**-Pd(dba) or the **1**-Pd series are both larger than those in the **4**-Pd series. These results show that the secondary Pd^0–arene interaction appears to stabilise the Pd-phosphine complexes despite the fact that **1e** has a smaller electron-donating ability than **4e**. The ordering of the ΔH and ΔG values of the complexes in all the series shows that Cy > Ph > BFPy, which matches with the ordering of the compounds based on the electron-donating ability of the phosphines. A comparison of the ΔH values in **4**-Pd and **1**-Pd gives the following values: $\Delta\Delta H$ = 8.5 (Cy), 9.1 (Ph) and 6.0 kcal/mol (BFPy). Although **1a** has a better electron-donating ability than **4a**, the comparisons of the incremental increase of $\Delta\Delta H$ give the smallest value. This indicates that the secondary Pd^0–arene interaction of **1a** is weaker than **1d** and **1e**. In fact, the distance between Pd and C(ortho) in **1**-Pd complex lengthens with an increase in the electron-withdrawing ability of the R group on the phosphorous of **1**: 2.286 (BFPy) > 2.220 (Ph) > 2.203 (Cy) Å (Fig. 2).

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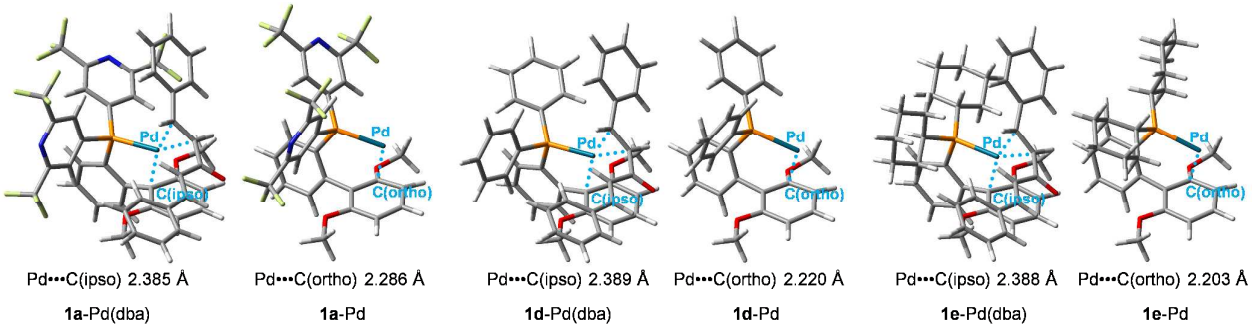

Fig. 2 Optimised structures of **1**-Pd(dba) and **1**-Pd complexes by oniom(mp2/lanl2dz:b3lyp/lanl2dz).

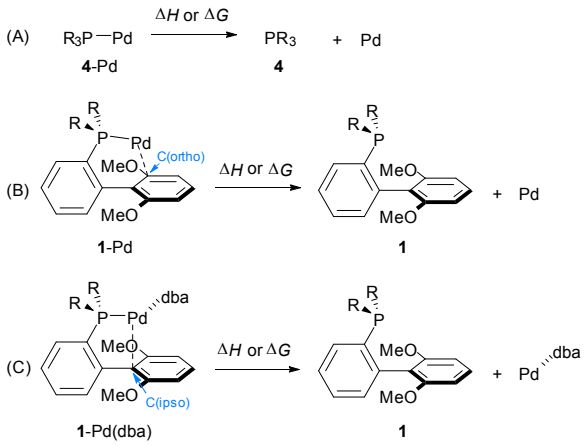

Table 3 The bond-dissociation energies (ΔH, ΔG) of **1**-Pd, **1**-Pd(dba) and **4**-Pd[a]

	BFPy (**a**)	Ph (**d**)	Cy (**e**)
(A) **4**-Pd			
Δ*H* (kcal/mol)	23.7	25.2	28.7
Δ*G* (kcal/mol)	15.0	16.6	20.4
(B) **1**-Pd			
Δ*H* (kcal/mol)	29.7	34.3	37.2
Δ*G* (kcal/mol)	22.4	24.6	27.0
(C) **1**-Pd(dba)			
Δ*H* (kcal/mol)	40.8	43.3	45.9
Δ*G* (kcal/mol)	25.4	28.7	31.0

[a] Optimization of structures and dissociation energies were calculated at the oniom(mp2/lanl2dz:b3lyp/ lanl2dz) level.

To further obtain information, we analysed the Pd^0–arene interaction using NBO methods at the M06-2X level with the basis sets of 6-31G(d) for C, H, O, F and P and LandL2DZ + ECP for Pd. Numerous orbital interactions show that over 1.0 kcal/mol of second-order perturbation energy was observed for all relevant Pd^0–ligand interactions. In all the **1**-Pd complexes, the following interactions were found: 1) P→Pd interaction of $Lp_P \rightarrow Lp^*_{Pd}$; 2) Pd→Ar interaction of $Lp_{Pd} \rightarrow \pi^*_{Ar}$ and 3) Ar→Pd interactions a) $\sigma_{Ar1} \rightarrow Lp^*_{Pd}$, b) $\sigma_{Ar2} \rightarrow Lp^*_{Pd}$, c) $\sigma_{Ar3} \rightarrow Lp^*_{Pd}$ and d) $\pi_{Ar} \rightarrow Lp^*_{Pd}$ (Fig. 3). In all the **1**-Pd(dba) complexes, the following interactions were found: 1) P→Pd interaction of $Lp_P \rightarrow Lp^*_{Pd}$; 2) Pd→Ar interactions of a) $Lp_{Pd1} \rightarrow \pi^*_{Ar}$, b) $Lp_{Pd2} \rightarrow \pi^*_{Ar}$ and c) $Lp_{Pd3} \rightarrow \pi^*_{Ar}$; 3) Ar→Pd interactions of a) $\sigma_{Ar1} \rightarrow Lp^*_{Pd}$, b) $\sigma_{Ar2} \rightarrow Lp^*_{Pd}$, c) $\sigma_{Ar3} \rightarrow Lp^*_{Pd}$, d) $\pi_{Ar} \rightarrow Lp^*_{Pd}$; 4) Pd→dba interaction of $Lp_{Pd} \rightarrow \pi^*_{dba}$ and 5) dba→Pd interactions of 1) $\sigma_{dba} \rightarrow Lp^*_{Pd}$, 2) $\pi_{dba} \rightarrow Lp^*_{Pd}$ (Fig. 4).

To conduct an energetic analysis of the listed interactions from 1) to 5), the deletion energies were calculated by combining the second-order perturbative estimates from each of these interactions (Table 4). The P→Pd interactions of the **1**-Pd(dba) (33.6–38.0 kcal/mol) or the **1**-Pd complexes (32.0–38.1 kcal/mol) are relatively small and have a narrow range relative to the **4**-Pd complexes (39.2–54.0 kcal/mol). In the cases of the **1**-Pd(dba) complexes, the 4) Pd→dba interaction (44.6–51.9 kcal/mol) is the strongest interaction[17] over the 1) P→Pd interaction (33.6–38.0 kcal/mol). The 2) Pd→Ar and 3) Ar→Pd interactions are only relevant to a secondary Pd^0–arene interaction. The 3) Ar→Pd interaction (12.4–12.7 kcal/mol) is stronger than the 2) Pd→Ar interaction (5.1–6.1 kcal/mol), which shows that the transfer of electrons from the aromatic ring to Pd is the dominant contributor towards the secondary Pd^0–arene interaction in **1**-Pd(dba) complexes. The 3) Ar→Pd interaction is relatively weak, and no marked differences are found for the substituent on the P atom (12.7 kcal/mol for BFPy vs. 12.4 kcal/mol for Ph vs. 12.5 kcal/mol for Cy). This is probably due to the dominance of the electron exchange between Pd and dba, 4) Pd→dba and 5) dba→Pd interactions. Next, we considered the **1**-Pd complexes, which

were the active species of the direct arylation reaction. In these cases, the secondary Pd^0–arene interactions are relatively strong. Note that the 2) Pd→Ar interactions (15.3–25.0 kcal/mol) are stronger than the 3) Ar→Pd interaction (14.6–18.3 kcal/mol), which indicates that the transfer of electrons from Pd to the aromatic ring is dominant in the secondary Pd^0–arene interaction in **1**-Pd complexes. These results run contrary to our expectations because it had been previously reported that the electron density at the metal centre increases due to palladium–arene interactions.[6b] Due to the transfer of electrons from Pd to the aromatic ring, the electron-donating **1e** provides the most favourable (25.0 kcal/mol) interaction, and the electron-poor **1a** provides the most unfavourable interaction (15.3 kcal/mol). This is observed because the electron density of Pd in **1**-Pd is increased by the electron-donating **1e**, and the electron density of Pd in **1**-Pd is less increased by the electron-poor **1a**. In the latter case, the strength of interaction 2) is similar to the 3) Ar→Pd interaction (14.6 kcal/mol). However, both interaction energies are larger than those in **1**-Pd(dba) complexes. Therefore, the secondary interaction can assist in sufficiently stabilising the active Pd^0 species even though **1a**-Pd has the weakest secondary Pd^0–arene interaction.

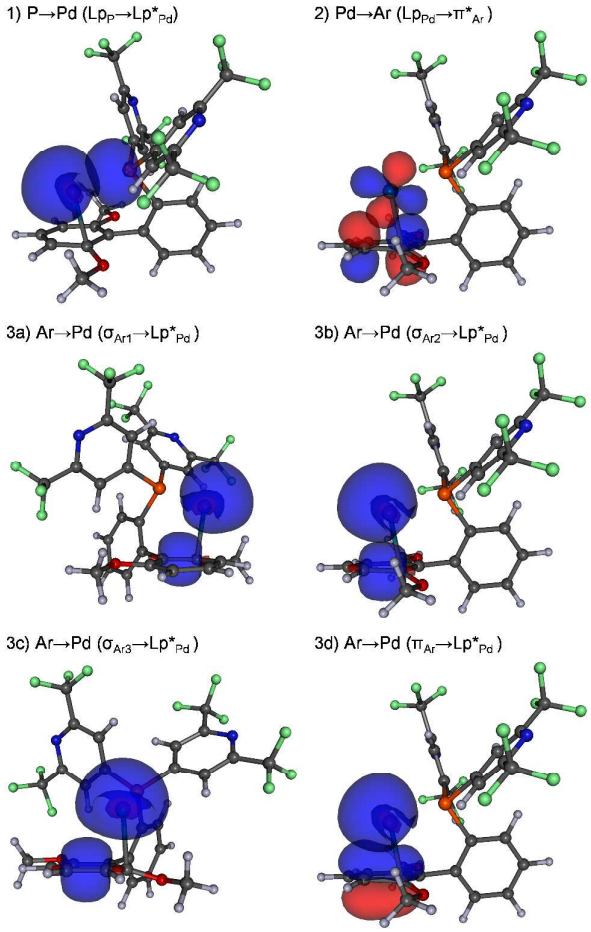

Fig. 3 Schematic presentation of orbital interactions showing over 1.0 kcal/mol of 2nd-order perturbation energy by NBO analysis at the M06-2X/6-31G(d) with LANL2DZ+ECP for interaction between Pd and phosphine in **1a**-Pd.

Table 4 Deletion energies for interaction with Pd[a]

	BFPy (**a**)	Ph (**d**)	Cy (**e**)
(A) **4**-Pd			
1) P→Pd	39.2[b]	47.1[b]	54.0[b]
(B) **1**-Pd			
1) P→Pd	32.0[b]	34.9[b]	38.1[b]
2) Pd→Ar	15.3[c]	23.1[c]	25.0[c]
3) Ar→Pd	14.6[d]	17.7[d]	18.3[d]
(C) **1**-Pd(dba)			
1) P→Pd	33.6[b]	35.9[b]	38.0[b]
2) Pd→Ar	6.0[e]	6.1[e]	5.1[e]
3) Ar→Pd	12.7[d]	12.4[d]	12.5[d]
4) Pd→dba	44.6[f]	51.0[f]	51.9[f]
5) dba→Pd	24.5[g]	25.5[g]	25.5[g]

[a] Deletion energies (kcal/mol) were calculated at the M06-2X/6-31G(d) with LandL2DZ + ECP. [b] Deletion energy of Lp$_P$→Lp*$_{Pd}$ interaction. [c] Deletion energy of Lp$_{Pd}$→π*$_{Ar}$ interaction. [d] Deletion energy of interactions: σ$_{Ar1}$→Lp*$_{Pd}$, σ$_{Ar2}$→Lp*$_{Pd}$, σ$_{Ar3}$→Lp*$_{Pd}$ and π$_{Ar}$→Lp*$_{Pd}$. [e] Deletion energy of interactions: Lp$_{Pd1}$→π*$_{Ar}$, Lp$_{Pd2}$→π*$_{Ar}$ and Lp$_{Pd3}$→π*$_{Ar}$. [f] Deletion energy of Lp$_{Pd}$→π*$_{dba}$ interaction. [g] Deletion energy of interactions: σ$_{dba}$→Lp*$_{Pd}$ and π$_{dba}$→Lp*$_{Pd}$.

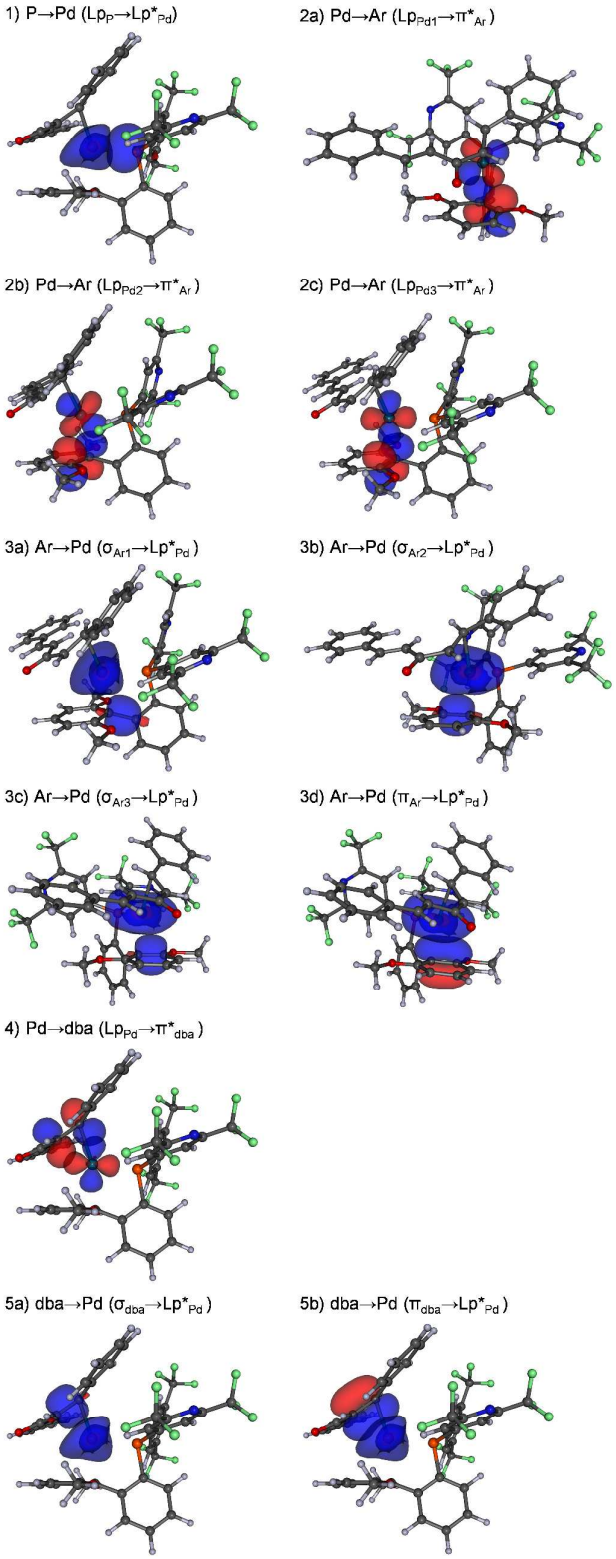

Fig. 4 Schematic presentation of orbital interactions showing over 1.0 kcal/mol of 2nd-order perturbation energy by NBO analysis at the M06-2X/6-31G(d) with LANL2DZ+ECP for interaction between Pd and phosphine or dba in **1a**-Pd(dba).

Conclusions

We synthesised novel, highly electron-poor Buchwald-type phosphines BFPySphos (**1a**), which accelerated the direct arylation of 2-propylthiophene in comparison to the known Buchwald-type ligands PhSPhos (**1d**) and SPhos (**1e**) or PR_3 (**4**). Although the catalytic activity for the direct arylation of 2-propylthiophene tends to increase with the electron-poor ability of ligands, the stability of the catalyst is also essential. Investigations on the secondary Pd^0–arene interaction of **1**-Pd using the NBO method clarified that a) the electron transfer from Pd to Ar is the dominant contributor towards the interaction, b) the secondary interaction of electron-poor **1a** is weak compared to PhSPhos (**1d**) and SPhos (**1e**) and c) this interaction in **1a** still has the capacity to sufficiently stabilise the active species of Pd^0.

Experimental

General information

All catalytic reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. All solvents were purchased as dehydrated grade from Kanto Chemical Co. and then were stored in Schlenk tubes under an argon atmosphere. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise noted. Preparative column chromatography was carried out by using silica gel (Kanto Chemical Co. 60N, 63-210 μm). ^{1}H NMR and ^{13}C NMR spectra were measured at 400 MHz and 100 MHz, respectively, and chemical shifts are given relative to tetramethylsilane (TMS). ^{31}P NMR spectra were measured at 162 MHz, and chemical shifts are given relative to 85% H_3PO_4. ^{19}F NMR spectra were measured at 376 MHz, and chemical shifts are given relative to CCl_3F using C_6F_6 as secondary reference (–162.9 ppm).

2-Bis[2,6-bis(trifluoromethyl)-4-pyridyl]phosphino-2',6'-dimethoxybiphenyl [BFPySPhos (1a)]

(2',6'-Dimethoxybiphenyl-2-yl)phosphine (**2**) (443.2 mg, 1.80 mmol) in a dried 50 mL Schlenk flask with argon was added triphosgene (587.5 mg, 1.98 mmol) and THF (17 mL). The reaction mixture was stirred at 50 °C overnight and subsequently cooled to room temperature. Concentration under vacuum gave the crude 2-dichlorophosphino-2',6'-dimethoxybiphenyl (**3**).

A dried 100 mL three-necked round-bottomed flask was flashed with argon and charged with magnesium (328.2 mg, 13.5 mmol), LiCl (286.1, 6.75 mmol) and Et_2O (16.5 mL). A solution of DIBAL in hexane (1.0 M, 85 μL, 0.085 mmol) was added and stirred for 15 min. Then 4-bromo-2,6-bis(trifluoromethyl)pyridine (1.59 g, 5.40 mmol) was added and reaction mixture was stirred for 90 min. After addition of a solution of crude **3** in THF (3 mL) at 0 °C, the mixture was stirred for 4 h at room temperature and then sat. NH_4Cl aq. was added. After extraction with EtOAc, and treated in a usual manner to give a crude product. The resulting solid was

purified by silica gel chromatography (hexane / EtOAc = 7 / 1) to give 555.4 mg of **1a** (46% yield) as a white solid. M.p. 143-144 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 - 7.58 (m, 5H), 7.48 – 7.32 (m, 3H), 7.04 – 7.00 (m, 1H), 6.60 (d, J = 8.4 Hz, 2H), 3.61 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.7, 152.5 (d, J_P = 26.2 Hz), 148.8 (dq, J_F = 35.7 Hz, J_P = 4.3 Hz), 143.2(d, J_P = 37.5 Hz), 133.9 (d, J_P = 1.1 Hz), 132.5 (d, J_P = 7.6 Hz), 132.0, 131.3 (d, J_P = 2.1 Hz), 130.6, 129.1, 126.1(d, J_P = 17.6 Hz), 120.8 (q, J_F = 273.4 Hz), 117.8 (d, J_P = 8.6 Hz), 103.9, 55.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ -69.1 (s). ^{31}P NMR (162 MHz, $CDCl_3$): δ -9.1 (s). IR (KBr): 2962, 2938, 2839, 1592, 1474, 1246, 1133, 764 cm^{-1}. HRMS (CI) m/z calcd for $C_{28}H_{17}F_{12}N_2O_2P$ ($[M+H]^+$): 673.0914, found : 673.0930.

2-Bis[3,5-bis(trifluoromethyl)phenyl]phosphino-2',6'-dimethoxybiphenyl [{3,5-$(CF_3)_2$-C_6H_3}SPhos (1b)]

The phosphine **1b** was obtained from **2** (240.3 mg, 0.976mmol) with triphosgene (317.5 mg, 1.07 mmol), and then 3,5-bis(trifluoromethyl)bromobenzene (500µL, 2.93 mmol) with magnesium (177.9 mg, 7.32 mmol) by the procedure described for **1a** (65% yield as a white solid). M.p. 116 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 2H), 7.62 (d, J = 6.0 Hz, 4H), 7.51 (dt, J = 7.6, 0.6 Hz, 1H), 7.40 – 7.26 (m, 3H), 7.07 – 7.02 (m, 1H), 6.56 (d, J = 8.4 Hz, 2H), 3.56 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.6, 142.1 (d, J_P = 35.6 Hz), 140.8 (d, J_P = 20.1 Hz), 134.1 (d, J_P = 6.1 Hz), 133.3 – 132.7 (m), 131.7 (dq, J_F = 33.0 Hz, J_P = 5.8 Hz), 131.7 (d, J_P = 6.7 Hz), 130.6, 130.0, 128.3, 123.1 (q, J_F = 271.3 Hz), 122.7 - 122.5 (m), 118.0 (d, J_P = 8.2 Hz), 103.5, 55.4. ^{19}F NMR (376 MHz,$CDCl_3$): δ -64.2 (s). ^{31}P NMR (162 MHz, $CDCl_3$): δ -9.2 (s). IR (KBr): 2976, 2844, 1591, 1468, 1359, 1109, 1035, 773 cm^{-1}. HRMS (CI) m/z calcd for $C_{30}H_{20}F_{12}O_2P$ ($[M+H]^+$): 671.1009, found : 671.1018.

***trans*-[RhCl(1a)$_2$CO]**

A 20 mL Schlenk flask was flushed with argon and charged with **1a** (50.0 mg, 74.4 µmol), $[RhCl(CO)_2]_2$ (8.0 mg, 20.6 µmol), and dichloromethane (1.0 mL). The solution was stirred at room temperature for 1 h. The solution was filtrated, and concentrated under reduced pressure to give *trans*-[RhCl(**1a**)$_2$CO] as a yellow solid. ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.1 (d, J = 137.8 Hz). IR (CH_2Cl_2): 2972, 2956, 2835, 2001, 1591, 1474, 1242, 1127, 780, 750 cm^{-1}.

***trans*-[RhCl(1b)$_2$CO]**

Synthesis of *trans*-[RhCl(**1b**)$_2$CO] were conducted by the procedure described for *trans*-[RhCl(**1a**)$_2$CO] using **1b** (50.0 mg, 74.6 µmol) and $[RhCl(CO)_2]_2$ (8.3 mg, 21.3 µmol). A yellow solid. ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.3 (d, J = 134.8 Hz). IR (CH_2Cl_2): 2972, 2841, 1991, 1599, 1474, 1354, 1112, 1097, 854, 596 cm^{-1}.

***trans*-[RhCl(1c)$_2$CO]**

Synthesis of *trans*-[RhCl(**1c**)$_2$CO] were conducted by the procedure described for *trans*-[RhCl(**1a**)$_2$CO] using **1c** (30.0 mg, 56.1 µmol) and $[RhCl(CO)_2]_2$ (5.5 mg, 14.1 µmol). A yellow solid. ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.5 (d, J = 132.9 Hz). IR (CH_2Cl_2): 3061, 2985, 2295, 1985, .01446, 1253, 1113, 788, 691 cm^{-1}.

***trans*-[RhCl(1d)$_2$CO]**

Synthesis of *trans*-[RhCl(**1d**)$_2$CO] were conducted by the procedure described for *trans*-[RhCl(**1a**)$_2$CO] using **1d** (50.0 mg, 125.4 µmol) and $[RhCl(CO)_2]_2$ (13.7 mg, 35.2 µmol). A yellow solid. ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.1 (d, J = 130.8 Hz). IR (CH_2Cl_2): 2992, 2936, 2837, 1979, 1591, 1462, 1254, 1113, 787, 686 cm^{-1}.

***trans*-[RhCl(1e)$_2$CO]**

Synthesis of *trans*-[RhCl(**1e**)$_2$CO] were conducted by the procedure described for *trans*-[RhCl(**1a**)$_2$CO] using **1e** (50.0 mg, 121.8 µmol) and $[RhCl(CO)_2]_2$ (12.1 mg, 31.1 µmol). A yellow solid. ^{31}P NMR (162 MHz, $CDCl_3$): δ 49.6 (d, J = 124.0 Hz). IR (CH_2Cl_2): 2974, 2938, 2853, 1959, 1589, 1429, 1251, 1113, 794, 743 cm^{-1}.

General Procedure for the direct arylation of 2-propylthiophene

A 10 mL Schlenk flask was flushed with argon and charged with K_2CO_3 (1.5 equiv), PivOH (30 mol%) and DMA (0.3 M). The mixture was stirred at room temperature for 30 min, and then $Pd(OAc)_2$ (1 mol%), ligand (2 mol%), 2-propylthiophene (1.2 equiv) and arylbromide (1.0 equiv) were added. The resulting mixture was stirred at 100 °C for 3 h. The reaction mixture was then poured into water and extracted with EtOAc. The organic layer were dried over Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by silica gel column chromatography with hexane to afford the corresponding product.

Pd/1a-catalyzed direct arylation of 2-propylthiophene with 4-bromobenzotrifluoride

The direct arylation of 2-propylthiophene (50 µL, 0.39 mmol) with 4-bromobenzotrifluoride (45 µL, 0.32mmol) were conducted using $Pd(OAc)_2$ (0.72 mg, 3.21 µmol), **1a** (4.32 mg, 6.42 µmol), K_2CO_3 (66.63 mg, 0.48 mmol), PivOH (9.85 mg, 0.096 mmol) and DMA (1.1 mL) by the general procedure to give 2-propyl-5-{4-(trifluoromethyl)phenyl}thiophene[18] as a white solid (77.74 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 3.6 Hz, 1H), 6.78 (d, J = 3.6 Hz, 1H), 2.81 (t, J = 7.5 Hz, 2H), 1.74 (sext, J = 7.4 Hz, 2H), 1.01 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 140.0, 138.2, 128.9 (d, J = 32.3 Hz), 127.8, 125.9 (q, J = 3.8 Hz), 125.6, 125.5, 124.3, 32.4, 25.0, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.6 (s).

2-Phenyl-5-propylthiophene[19]

The direct arylation of 2-propylthiophene (52 µL, 0.40 mmol) with bromobenezene (52 µL, 0.33mmol) were conducted using $Pd(OAc)_2$ (0.75 mg, 3.34 µmol), **1a** (4.49 mg, 6.68 µmol), K_2CO_3 (69.24 mg, 0.50 mmol), PivOH (10.23 mg, 0.10 mmol) and DMA (1.1 mL) by the general procedure to give 2-phenyl-5-propylthiophene as a colorless oil (59.93 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 7.4 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.24 (d, J = 8.2 Hz, 1H),

7.12 (d, *J* = 3.5 Hz, 1H), 6.74 (d, *J* = 3.5 Hz, 1H), 2.80 (t, *J* = 7.5 Hz, 2H), 1.73 (sext, *J* = 7.4 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 145.6, 141.8, 134.9, 128.9, 127.1, 125.6, 125.6, 125.2, 122.8, 32.4, 25.0, 13.8.

2-(4-Methylphenyl)-5-propylthiophene[18]

The direct arylation of 2-propylthiophene (50 µL, 0.39 mmol) with 4-bromotoluene (54.97 mg, 0.32mmol) were conducted using $Pd(OAc)_2$ (0.72 mg, 3.21 µmol), **1a** (4.32 mg, 6.42 µmol), K_2CO_3 (66.63 mg, 0.48 mmol), PivOH (9.85 mg, 0.096 mmol) and DMA (1.1 mL) by the general procedure to give 2-(4-methylphenyl)-5-propylthiophene as a colorless oil (56.53 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.44 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 3.6 Hz, 1H), 6.72 (d, *J* = 3.5 Hz, 1H), 2.78 (t, *J* = 7.7 Hz, 2H), 2.34 (s, 3H), 1.71 (sext, *J* = 7.5 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 145.0, 142.0, 136.9, 132.1, 129.6, 125.5, 125.1, 122.2, 32.4, 25.0, 21.3, 13.9.

2-Methyl-5-{4-(trifluoromethyl)phenyl}thiophene[20]

The direct arylation of 2-methylthiophene (37.5 µL, 0.39 mmol) with 4-bromobenzotrifluoride (45µL, 0.32mmol) were conducted using $Pd(OAc)_2$ (0.72 mg, 3.21 µmol), **1a** (4.32 mg, 6.42 µmol), K_2CO_3 (66.63 mg, 0.48 mmol), PivOH (9.85 mg, 0.096 mmol) and DMA (1.1 mL) by the general procedure to give 2-methyl-5-{4-(trifluoromethyl)phenyl}thiophene as a white solid (69.84 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.65 – 7.56 (m, 4H), 7.20-7.18 (m, 1H), 6.77 - 6.75 (m, 1H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 141.3, 140.3, 138.2, 129.5 – 128.2 (m), 126.7, 126.0 (q, *J* = 3.8 Hz), 125.5, 124.5, 124.4 (q, *J* = 270.0 Hz), 15.7. ^{19}F NMR (376 MHz, $CDCl_3$): *δ* -63.6 (s).

2-{4-(Trifluoromethyl)phenyl}benzo[*b*]thiophene[12b]

The direct arylation of 2-methylthiophene (37.5 µL, 0.39 mmol) with 4-bromobenzotrifluoride (45µL, 0.32mmol) were conducted using $Pd(OAc)_2$ (0.72 mg, 3.21 µmol), **1a** (4.32 mg, 6.42 µmol), K_2CO_3 (66.63 mg, 0.48 mmol), PivOH (9.85 mg, 0.096 mmol) and DMA (1.1 mL) by the general procedure to give 2-{4-(trifluoromethyl)phenyl}benzo[*b*]thiophene as a white solid (77.55 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.87 – 7.79 (m, 4H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.64 (s, 1H), 7.41 – 7.33 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 142.4, 140.5, 139.9, 137.9, 131- 129.0 (m), 126.8, 126.2 – 126.0 (m), 125.1, 125.0, 124.1 (q, *J* = 270.4 Hz), 124.1, 122.5, 121.2. ^{19}F NMR (376 MHz, $CDCl_3$): *δ* -63.8 (s).

Evaluation of Kinetic Isotope Effect

A 10 mL Schlenk flask was flushed with argon and charged with K_2CO_3 (66.63 mg, 0.48 mmol), PivOH (9.84 mg, 0.096 mmol) and DMA (1.1 mL). The mixture was stirred at room temperature for 30 min., and then $Pd(OAc)_2$ (0.72 mg, 3.21 µmol), **1a** (4.32 mg, 6.42 µmol), 4-bromobenzotrifluoride (4.5 µL, 0.032mmol) and the 1 : 1 mixture of 2-propylthiophene and 2-propylthiophene-*d* (42 µL, 3.21 mmol) were added. The resulting mixture was stirred at 100 °C for 20 min. The reaction mixture was then poured into water and extracted with Et_2O. The organic layer were dried over Na_2SO_4 and concentrated under reduced pressure. The KIE is calculated by ^{1}H NMR.

Computational methods

The geometries of the phosphines (**1a**, **1d**, **1e**, **4a**, **4d** and **4e**) and their ligated Pd complexes (**1**-Pd, **1**-Pd(dba), and **4**-Pd) were fully optimized and characterized by frequency calculation by ONIOM method[21] at the second order Møller-Plesset perturbation method (MP2)[22] in the high-level layer and B3LYP (Becke's three parameter hybrid method[23a] using the Lee–Yang–Parr correlation function[23b]) density functional theory (DFT) in the low-level layer with the LANL2DZ basis set[24] using Gaussian 09 program.[25] The atom distribution in those two layers is as follows: high level layer is the atoms being related to the interaction with Pd, and the others are low level layer (the details are shown in ESI). Free energies and enthalpies (298.15 K, 1 atm) were computed for the gas phase. NBO calculations[26] were performed at the M06-2X[27] with 6-31G(d)[24] and LANL2DZ with effective core potential (ECP) for Pd. For the NBO energetic analysis, NBO deletions were employed using $DEL Keylist.[28]

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The acknowledgements come at the end of an article after the conclusions and before the notes and references.

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