

# Suzuki coupling catalyzed by a homoleptic Pd(I)–Pd(I) solvento complex

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## Abstract

The Pd<sup>I</sup>–Pd<sup>I</sup> bonded complex [Pd<sub>2</sub>(CH<sub>3</sub>CN)<sub>6</sub>][SbF<sub>6</sub>]<sub>2</sub> is catalytically active towards Suzuki cross-coupling reactions of aryl bromides or chlorides with various arylboronic acids under mild conditions giving good to excellent yields. Its performance is enhanced by the introduction of stoichiometric or limited phosphines. The effects of different ligands, metal oxidation states [Pd(II), Pd(I)Pd(0)], bases and solvents have been examined.

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**Keywords:** Suzuki coupling; Palladium; Dinuclear; Homoleptic; Catalyst

## 1. Introduction

Metal-catalyzed Suzuki coupling is one of the most powerful methodologies developed for C–C bond formation reactions [1,2]. In most cases, Pd(II) or Pd(0), supported by strong ligands such as phosphine [e.g., PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> or Pd(OAc)<sub>2</sub> + PPh<sub>3</sub>], is the catalyst of choice. Although dinuclear Pd(I) is well known in small molecular activation [3], its value in catalysis is only beginning to emerge [4] and its activity towards Suzuki coupling is largely unknown. Two of the rare examples are found in the recent work by Barder et al. [4b] and Weissman et al. [4d], both of them reported the use of phosphine arene-ligated Pd(I) dimer to promote Suzuki reaction. The former attributed the activity to the disproportionation of Pd(I) to the catalytically active Pd(II) and Pd(0). It is still unclear if Pd(I) serves an intermediate role in any of the key steps (oxidative addition, transmetallation and reductive elimination) in the catalytic cycle.

Accordingly, we are interested in the catalytic chemistry of Pd(I) complexes. As part of our current interest in cata-

lysts with hemilabile ligands, we are especially interested in ligands that are weak donor, or better still, “ligandless” catalysts. We have chosen the homoleptic complex [Pd<sub>2</sub>(CH<sub>3</sub>CN)<sub>6</sub>][BF<sub>4</sub>]<sub>2</sub>, earlier reported by Murahashi et al. [5,6] as a model since it meets our requirement. To minimize the anionic participation and possibility of metal coordination, we have modified the method and isolated the SbF<sub>6</sub><sup>−</sup> salt, *viz.* [Pd<sub>2</sub>(CH<sub>3</sub>CN)<sub>6</sub>][SbF<sub>6</sub>]<sub>2</sub> (**1**). We herein report its Suzuki activities towards the coupling of aryl bromides and chlorides with various arylboronic acids, under ligandless conditions and in the presence of phosphine ligands. The use of ligandless catalysts has attracted some recent attention because it could side-step problems such as product contamination by the adventitious ligands, high toxicity and cost of many ligands, side reactions between the ligand and substrate, etc. This study also provides an opportunity to examine the different effects of Pd(II), Pd(I) and Pd(0) on the catalytic performance towards Suzuki coupling.

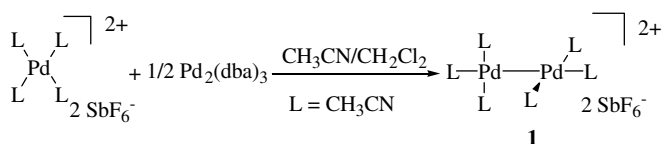
## 2. Results and discussion

The synthesis of **1** resembles that of the BF<sub>4</sub><sup>−</sup> analogue [6]. It is prepared from a redox coupling reaction of [Pd(CH<sub>3</sub>CN)<sub>4</sub>][SbF<sub>6</sub>]<sub>2</sub> with Pd<sub>2</sub>(dba)<sub>3</sub> (Scheme 1).

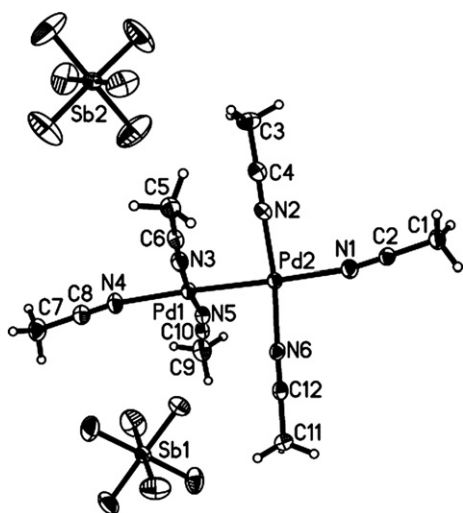
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Single-crystal crystallographic analysis of **1** reveals a similar mono-cationic dinuclear structure as the  $\text{BF}_4^-$  analogue [5]. The  $\text{Pd}_2$  core is stabilized only by terminal  $\text{CH}_3\text{CN}$  ligands, with little interaction with the counter-cation  $\text{SbF}_6^-$  (Fig. 1; Table 1). The Pd–Pd bond [2.4871(5) Å] is statistically identical to that of the  $\text{BF}_4^-$  analogue [2.486(1) Å] [5] and the mixed-ligand counterpart  $[\text{Pd}_2(\text{CH}_3\text{CN})_4(\text{PPh}_3)_2][\text{PF}_6]_2$  [2.4878(7) Å] [7]. These Pd–Pd bonds are among the strongest in  $\text{Pd}^I$ – $\text{Pd}^I$  bonded species, including  $[\text{Pd}_2(\text{C}_4\text{H}_6)_2(\text{PPh}_3)_2][\text{PF}_6]_2$  [Pd–Pd 3.1852(6) Å] [7]. One major difference between **1** and its  $\text{BF}_4^-$  counterpart is in the dihedral angle between the Pd coordination plane ( $69.2^\circ$  in **1** and  $75.5^\circ$  in the  $\text{BF}_4^-$  complex). The larger size of the anion has also significantly lengthened the intermolecular Pd···Pd separation from 5.735 Å in  $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$  [5] to 7.269 Å in **1**.



Scheme 1.

Fig. 1. Molecular structure of  $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{SbF}_6]_2$  (**1**). Thermal ellipsoids are drawn at the 30%.Table 1  
Selected bond lengths (Å) and angles ( $^\circ$ ) for **1**

Bond lengths			
Pd(1)–Pd(2)	2.4871(5)	Pd(1)–N(3)	1.985(4)
Pd(1)–N(5)	2.002(4)	Pd(1)–N(4)	2.155(4)
Pd(2)–N(1)	2.157(4)	Pd(2)–N(2)	1.987(5)
Pd(2)–N(6)	1.994(5)		
Bond angles			
N(3)–Pd(1)–Pd(2)	84.28(12)	N(5)–Pd(1)–Pd(2)	90.73(11)
N(4)–Pd(1)–Pd(2)	176.89(14)	N(2)–Pd(2)–Pd(1)	86.95(12)
N(6)–Pd(2)–Pd(1)	85.68(11)	N(1)–Pd(2)–Pd(1)	175.28(12)
N(1)–C(2)–C(1)	178.9(6)	N(2)–C(4)–C(3)	178.4(7)
N(3)–C(6)–C(5)	179.1(6)	N(4)–C(8)–C(7)	179.6(7)
N(5)–C(10)–C(9)	179.0(6)	N(6)–C(12)–C(11)	179.7(6)

Table 2

Suzuki cross-coupling of aryl bromides with boronic acids catalyzed by complex **1**<sup>a</sup>

$$\text{R}_1\text{-C}_6\text{H}_4\text{-Br} + \text{R}_2\text{-C}_6\text{H}_4\text{-B(OH)}_2 \xrightarrow[\text{r. t., 1 h}]{1.5 \text{ mol } \% \text{ cat. } \mathbf{1}, 2.4 \text{ equiv base}} \text{R}_1\text{-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-R}_2$$

Entry	Aryl bromide	Boronic acid	Yield/% <sup>b</sup>
1			100
2			81
3			100
4			63
5			67, 77 <sup>c</sup>
6			62, 80 <sup>c</sup>
7			97
8			70
9			74
10			65
11			66
12			88
13			62, 98 <sup>c</sup>
14			75
15			41, 92 <sup>c</sup>
16			49, 93 <sup>c</sup>
17			2, 15 <sup>c</sup>
18			<2

<sup>a</sup> Base is  $\text{K}_2\text{CO}_3$ .<sup>b</sup> Isolated yield.<sup>c</sup> Base is  $\text{Cs}_2\text{CO}_3$ .

The activities of  $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{SbF}_6]_2$  towards the cross-coupling of a number of aryl bromides with arylboronic acids at r.t. are given in Table 2. It is generally active

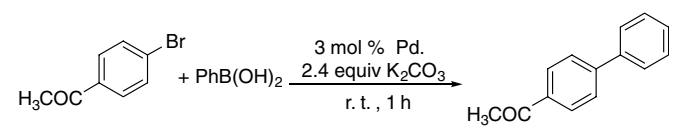
towards deactivated, electron-rich arylboronic acids (e.g. entry 12) and activated, electron-poor ones (e.g. entry 7), giving high yields under facile conditions. However, electron-rich aryl bromides show much poorer activities (e.g. entry 17). Use of  $\text{Cs}_2\text{CO}_3$  generally results in higher yields than  $\text{K}_2\text{CO}_3$  (e.g. entries 13 and 15–17). *Para*-substitution in aryl bromides generally show higher activity than corresponding *ortho*-substituents (e.g. entries 2 and 5). These coupling reactions proceed readily at r.t. achieving maximum yields within a short reaction duration (1 h). It is however not active towards aryl chlorides at r.t. (e.g. entry 18).

In a typical coupling reaction between 2-bromobenzonitrile and phenylboronic acid in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (1:1), using **1** as catalyst without addition of any ligand, the yields are 2%, 32%, 67% and 77% when the base is KF, CsF,  $\text{K}_2\text{CO}_3$  and  $\text{Cs}_2\text{CO}_3$ , respectively. The stronger base (in aqueous medium) *viz.*  $\text{CO}_3^{2-}$  performs better than  $\text{F}^-$ . This is unexpected since KF is a common and effective base for  $\text{Pd}_2(\text{dba})_3$ /phosphine catalysed Suzuki-type reactions [8,9]. This may be explained by the strong Pd–F bond which may impede the transmetalation.  $\text{Cs}_2\text{CO}_3$  gives the highest yield, which is also observed in some other systems [10].

The solvent effect is examined using the model coupling reaction between 4-bromoacetophenone and phenylboronic acid (Table 3). As expected, reaction in  $\text{CH}_3\text{CN}$  gives better yields than that in THF or MeOH, suggesting the stabilizing effect of the solvent ligand. Unexpectedly, addition of  $\text{H}_2\text{O}$  to all three solvents would significantly raise the yields. In the case of THF and  $\text{CH}_3\text{CN}$ , the yields become quantitative. It may have suppressed the trimerization of aryl boronic acid. It could also help in the solubilization of the inorganic base.

The catalytic performance of **1** is compared with its  $\text{BF}_4^-$  analogue and other common Pd(II) and Pd(0) complexes. This is performed on the model coupling between 4-bromoacetophenone and phenylboronic acid in  $\text{CH}_3\text{CN}-\text{H}_2\text{O}$  at r.t. for 1 h (Table 4). It is surprising that the seemingly non-coordinating anion could have a significant effect on the yield, as evident from the higher yield for **1** (entry 3) than its  $\text{BF}_4^-$  counterpart (entry 4). The lower stability of

Table 4

Influence of different catalysts on the coupling reaction<sup>a</sup>


Entry	Catalyst	Isolated yield (%)
1	$\text{Pd}(\text{OAc})_2$	100
2	$[\text{Pd}(\text{CH}_3\text{CN})_4][\text{SbF}_6]_2$	95
3	$[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{SbF}_6]_2$	100, 50 <sup>b</sup>
4	$[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$	57
5	$[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{SbF}_6]_2/\text{dppm}$	63 <sup>c</sup>
6	$[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{SbF}_6]_2/\text{dppf}$	98 <sup>c</sup>
7	$[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{SbF}_6]_2/\text{PPh}_3$	90 <sup>c</sup> , 13 <sup>d</sup>
8	$\text{Pd}_2(\text{dba})_3$	6
9	$\text{Pd}/\text{C}$	4

<sup>a</sup> All the catalytic loadings are expressed on a “per-palladium center” basis, solvents are  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (v/v = 1:1).

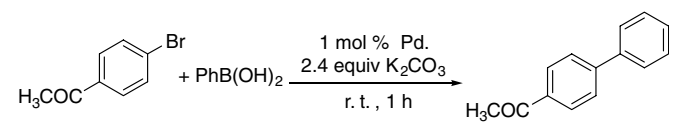
<sup>b</sup> Catalyst load is reduced to 2 mol%.

<sup>c</sup> Catalyst load is reduced to 2 mol%, free phosphine is added to give a ratio of Pd:P = 1:1.

<sup>d</sup> Catalyst load is reduced to 2 mol%, free phosphine is added to give a ratio of Pd:P = 1:3.

the  $\text{SbF}_6^-$  salt (**1**) seems to be associated with its higher activity. Comparison with the analogous homoleptic complex of Pd(II) i.e.  $[\text{Pd}(\text{CH}_3\text{CN})_4]^{2+}$  (entry 2) shows that they are similar, perhaps supporting the idea that disproportionation [of Pd(I) to Pd(II) + Pd(0)] provides a key entry to the catalytic cycle. The importance of Pd(I) or Pd(II) is exemplified when metallic Pd (entry 9) or Pd(0) such as  $\text{Pd}_2(\text{dba})_3$  (entry 8), which usually shows high activities in other systems [8,11], are poor under our conditions.

Table 5

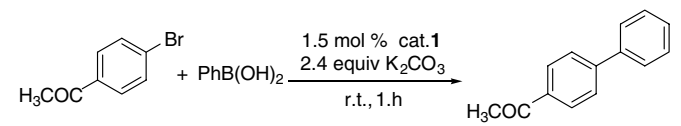
Influence of different ligands on the coupling reaction<sup>a</sup>


Entry	Ligand <sup>b</sup>	Isolated yield/%
1	$\text{PCy}_3$	87
2	$\text{PPh}_3$	90
3	$\text{P}(\text{OCH}_3)_3$	86
4	$\text{P}(n\text{-Bu})_3$	2
5	$\text{P}(t\text{-Bu})_3$	33
6	$\text{P}(3\text{-CH}_3\text{-Ph})_3$	34
7	$\text{P}(4\text{-CH}_3\text{O-Ph})_3$	60
8	$\text{P}(o\text{-tolyl})_3$	100
9	$(\eta\text{-C}_5\text{H}_4\text{-PCy}_2)\text{FeCp}$	100
10	Dppm	63
11	Dppe	6
12	Dppp	Trace
13	Dpph	81
14	$[\eta\text{-C}_5\text{H}_4\text{-P}(i\text{-Pr})_2]_2\text{Fe}$	76
15	$[\eta\text{-C}_5\text{H}_4\text{-PEt}_2]_2\text{Fe}$	65
16	$[\eta\text{-C}_5\text{H}_4\text{-PPh}_2]_2\text{Fe}$	98

<sup>a</sup> Free phosphine is added to give a ratio of Pd(I)/P (of ligand) = 1:1.

Table 3

Effect of the solvent on the coupling reaction



Entry	Solvent <sup>a</sup>	Isolated yield (%)
1	THF	20
2	MeOH	24
3	$\text{CH}_3\text{CN}$	58
4	$\text{THF}-\text{H}_2\text{O}$	100
5	$\text{MeOH}-\text{H}_2\text{O}$	67
6	$\text{CH}_3\text{CN}-\text{H}_2\text{O}$	100

<sup>a</sup> For mixed solvent, v/v = 1:1.

Table 6  
Suzuki cross-coupling of aryl chlorides with boronic acids<sup>a</sup>

Entry	Aryl chloride	Boronic acid	Ligand <sup>b</sup>	Yield/ %
1				74
2				63
3				56
4				97
5				98
6			$[\eta\text{-C}_5\text{H}_4\text{-P}(t\text{-Bu})_2]_2\text{Fe}$	97, 20 <sup>b</sup>
7			PPhCy <sub>2</sub>	80
8			P( <i>t</i> -Bu) <sub>3</sub>	38
9			$[\eta\text{-C}_5\text{H}_4\text{-P}(t\text{-Bu})_2]_2\text{Fe}$	90
10			$[\eta\text{-C}_5\text{H}_4\text{-P}(t\text{-Bu})_2]_2\text{Fe}$	100
11			$[\eta\text{-C}_5\text{H}_4\text{-P}(t\text{-Bu})_2]_2\text{Fe}$	20
12			$[\eta\text{-C}_5\text{H}_4\text{-P}(t\text{-Bu})_2]_2\text{Fe}$	68
13			$[\eta\text{-C}_5\text{H}_4\text{-P}(t\text{-Bu})_2]_2\text{Fe}$	34
14			$[\eta\text{-C}_5\text{H}_4\text{-P}(t\text{-Bu})_2]_2\text{Fe}$	23

<sup>a</sup> Reaction conditions: 0.5 mmol of aryl chloride, 0.67 mmol of aryl boronic acid, 1.2 mmol of Cs<sub>2</sub>CO<sub>3</sub>, 0.01 mmol of complex 1, Pd(I)/P (of ligand) = 1:1, solvent mixture is CH<sub>3</sub>CN/H<sub>2</sub>O (v/v = 1:1); isolated yield.

<sup>b</sup> Free phosphine is added to give a ratio of Pd(I)/P (of ligand) = 1:2.

These experiments also suggested that the metallic Pd or Pd(0) is unlikely the major active catalyst for **1** to be used as catalyst in this system.

Complex **1** is an effective catalyst in bromide coupling at r.t., but it is handicapped by its partial decomposition (to colloidal metal) during the catalytic reactions. Such decomposition is not surprising since there is no strong ligand that can hold the dimetal core together and keep it in solution, especially if it reduces to Pd(0). This problem can be significantly alleviated by introducing a stoichiometric and limited quantity of an appropriate phosphine ligand to the catalyst mixture. Indeed, when PPh<sub>3</sub> (entry 7), dppm (entry 5) or dppf (entry 6) is introduced to the catalyst mixture, we witnessed substantially less decomposition and accordingly high product yields when the catalyst load is reduced to 2 mol%. Another advantage of this system is that with the use of **1** as a pre-catalyst, one can introduce and measure an exact quantity of any ligand in support. For example, PPh<sub>3</sub> can be added in threefold excess. This evidently reduces the extent of catalyst decomposition, but this would over-saturate the metal and render it less effective as a catalyst (entry 7).

A comparison of different ligands in supporting complex **1** is listed in Table 5. The catalyst load is reduced to 1 mol% whereas the reaction is kept at r.t. Some of the phosphine ligands have been successfully used to catalyze Suzuki coupling with Pd(0) [12,13]. It is evident that in the majority of cases, **1** would perform better in the presence of a supporting mono- or diphosphine. For example, the reaction of 4-bromoacetophenone with phenylboronic acid gives only 50% completion in the ligand-free system under the specific experimental conditions (Table 4, entry 3). In the presence of P(*o*-tolyl)<sub>3</sub> or [η-C<sub>5</sub>H<sub>4</sub>-PCy<sub>2</sub>]<sub>2</sub>Fe[η-C<sub>5</sub>H<sub>5</sub>], the yield is quantitative (entries 8 and 9). The latter is a surprise since it shows poor activity in conjunction with Pd<sub>2</sub>(dba)<sub>3</sub> system [12], but with **1**, it is very effective (entry 9). In general, the more sterically demanding phosphines for both alkyl, and ferrocenyl-based ligands tend to give better yields. For example, P(*t*-Bu)<sub>3</sub> is significantly better than P(*n*-Bu)<sub>3</sub> (entries 4 and 5) whereas [η-C<sub>5</sub>H<sub>4</sub>-P(*i*-Pr)<sub>2</sub>]<sub>2</sub>Fe is better than (η-C<sub>5</sub>H<sub>4</sub>-PEt<sub>2</sub>)<sub>2</sub>Fe (entries 14 and 15). For diphosphines, dppm and dpph (entries 10 and 13) are superior than dppe and dppp (entries 11 and 12). The ability of dppm to support dinuclear structure such as A-frame and side-by-side structure is well known. It could hence offer the best stabilizing support for **1**. For dpph, it tends to give more stable bridging structure with non-interacting metals. If **1** undergoes disproportionation, the Pd–Pd bond is likely to be cleaved. Presence of dpph could help to keep the metals in solution in form of Pd(II)–dpph–Pd(II) or even Pd(II)–dpph–Pd(0) pairs.

We decided to challenge the more demanding coupling using aryl chlorides. Complex **1** is kept at 2 mol% and supported by a suitable ligand. (Table 6) The reaction is run at a manageable 70 °C overnight. In agreement with the bromide substrates (Table 5), and our earlier work in the P/P, P/O and P/N ligands [12,13], the ferrocenyl-based ligands

are most effective. Both ferrocenyl and aryl-based ligands (entries 5 and 7) are better than alkyl-substituted phosphine (entry 8). In some of the ferrocene-based ligands, the yields are near-quantitative (entries 4–6 and 10). This may be attributed to a better stereogeometrical mobility and coordination flexibility that is inherent of the ferrocenyl moiety. The ferrocenyl moiety also provides a better electronic buffer than the alkyl or aryl. A direct comparison between FcPCy<sub>2</sub> and PhPCy<sub>2</sub> suggests that the former gives near-quantitative yield whereas the latter reaches 80%. (entries 5 and 7). Contrary to our earlier work on Pd(0) [12], the performance of FcPCy<sub>2</sub> (entry 5) is matching that of the P/O ligand acetal ligand (entry 4). It further suggests that the Pd(I) in **1** functions differently from other Pd(0) catalysts.

In our earlier study on P/N ferrocenyl ligand [13], we suggested that the stronger donation of an alkyl substituent (compared to aryl) can help the imine [η-C<sub>5</sub>H<sub>4</sub>CH=NCH(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>)]Fe[η-C<sub>5</sub>H<sub>4</sub>P(*t*-Bu)<sub>2</sub>] promote the oxidative addition intermediate better than [η-C<sub>5</sub>H<sub>4</sub>CH=N(C<sub>6</sub>H<sub>5</sub>)]Fe[η-C<sub>5</sub>H<sub>4</sub>P(*t*-Bu)<sub>2</sub>] (entries 1 and 2). This is also evident here as [η-C<sub>5</sub>H<sub>4</sub>P(*t*-Bu)<sub>2</sub>]<sub>2</sub>Fe is also very effective (entry 6). In general, the P/P and P/O ferrocenyl-based ligands perform better than the P/N (entries 1, 4 and 5). Consistent with the observations in the bromide substrates, the efficiency of aryl chloride activation and subsequent coupling also drops significantly when the P:Pd ratio is increased from 1 to 2 (entry 6). In general, a mixture of **1** and [η-C<sub>5</sub>H<sub>4</sub>P-*t*-Bu)<sub>2</sub>]<sub>2</sub>Fe is effective towards a range of aryl substrates at 70 °C in the presence of Cs<sub>2</sub>CO<sub>3</sub>, giving high to moderate yields (Table 6).

### 3. Conclusion

[Pd<sub>2</sub>(CH<sub>3</sub>CN)<sub>6</sub>][SbF<sub>6</sub>]<sub>2</sub> is an effective pre-catalyst in Suzuki coupling towards a range of aryl bromides at r.t. and chlorides at 70 °C, giving near-quantitative yields in many cases. Its use provides an alternative to the conventional use of Pd(II) or Pd(0) in a range of C–C cross-coupling reactions. A key advantage of using such complex is that we could conveniently introduce different types of donor ligands L to the reaction mixture to generate [Pd<sub>2</sub>(CH<sub>3</sub>CN)<sub>5</sub>L]<sup>2+</sup> or [Pd<sub>2</sub>(CH<sub>3</sub>CN)<sub>4</sub>L<sub>2</sub>]<sup>2+</sup>, etc., or using anionic ligands X to give [Pd<sub>2</sub>(CH<sub>3</sub>CN)<sub>5</sub>X]<sup>+</sup> or Pd<sub>2</sub>(CH<sub>3</sub>CN)<sub>4</sub>X<sub>2</sub>, etc. *in situ*. This would provide a convenient access to a range of Pd<sup>I</sup>–Pd<sup>I</sup> catalysts without the need to undergo extensive independent syntheses for such compounds. It is currently unclear on the role of the strong Pd<sup>I</sup>–Pd<sup>I</sup> bond in this catalysis. One assumption is that oxidative addition and reductive elimination occur across the Pd–Pd bond. The other possibility is that entering the catalytic cycle is preceded by disproportionation of the dinuclear core to perhaps mononuclear Pd(II) and Pd(0). We are especially interested to trap any reaction intermediates that can be stabilized by the addition of free mono or diphosphine. Their use leads not only to better product yields, but also higher chance to isolate more stable inter-

Table 7  
Selected crystal data, data collection and refinement parameters of compound **1**

Compound	<b>1</b> · (CH <sub>3</sub> CN) <sub>2</sub>
Formula	C <sub>16</sub> H <sub>24</sub> F <sub>12</sub> N <sub>8</sub> Pd <sub>2</sub> Sb <sub>2</sub>
Formula weight	1012.73
Crystal size (mm)	0.50 × 0.36 × 0.10
Temperature (K)	223(2)
Crystal system	Monoclinic
Space group	<i>P</i> 2(1)/ <i>c</i>
<i>a</i> (Å)	15.1495(8)
<i>b</i> (Å)	9.9600(5)
<i>c</i> (Å)	21.8682(12)
$\alpha$ (°)	90
$\beta$ (°)	105.0920(10)
$\gamma$ (°)	90
<i>V</i> (Å <sup>3</sup> )	3185.9(3)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	2.111
Radiation used	Mo K $\alpha$
$\mu$ (mm <sup>-1</sup> )	2.879
$\theta$ Range (°)	1.39–27.50
Number of unique reflections measured	21971
Maximum and minimum transmissions	0.7617 and 0.3270
Final <i>R</i> indices [ <i>I</i> > 2 · $\sigma$ ( <i>I</i> )] <sup>a,b</sup>	<i>R</i> <sub>1</sub> = 0.0454, <i>wR</i> <sub>2</sub> = 0.0972
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0639, <i>wR</i> <sub>2</sub> = 0.1040
Goodness-of-fit on <i>F</i> <sup>2c</sup>	1.054
Large difference in peak and hole (e Å <sup>-3</sup> )	1.381 and -0.496

$$^a R = (\sum |F_o| - |F_c|) / \sum |F_o|$$

$$^b wR_2 = [(\sum \omega |F_o| - |F_c|)^2 / \sum \omega |F_o|^2]^{1/2}$$

$$^c \text{Goodness-of-fit} = [(\sum \omega |F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{param}})]^{1/2}$$

mediates. Our current experiments are directed towards such goal.

#### 4. Experimental

General considerations. All chemical syntheses are carried out under N<sub>2</sub> using conventional Schlenk techniques, unless otherwise indicated.

Suzuki reaction. In a typical procedure for ligand free system, a suspension of [Pd<sub>2</sub>(CH<sub>3</sub>CN)<sub>6</sub>][SbF<sub>6</sub>]<sub>2</sub> (7 mg, 0.0075 mmol) in CH<sub>3</sub>CN–H<sub>2</sub>O (*v/v* = 1:1) (4 ml) containing K<sub>2</sub>CO<sub>3</sub> (166 mg, 1.2 mmol), 4-bromo-acetophenone (100 mg, 0.5 mmol) and phenylboronic acid (78 mg, 0.65 mmol) was stirred for 1 h at r.t. under ambient pressure of N<sub>2</sub>. The solvent was then removed under reduced pressure. The resultant residual mixture was diluted with H<sub>2</sub>O (10 ml) and Et<sub>2</sub>O (10 ml), followed by extraction twice with Et<sub>2</sub>O. The ethereal extract was collected and stripped of solvent under vacuum. The product was isolated by column chromatography on silica, with hexanes/ethyl acetate as eluent, to give 99 mg (yield 100%) of 4-acetylbiphenyl as a solid which analyzed by GC/MS.

In a typical procedure for ligand system, a suspension of [Pd<sub>2</sub>(CH<sub>3</sub>CN)<sub>6</sub>][SbF<sub>6</sub>]<sub>2</sub> (9.5 mg, 0.01 mmol) and [η-C<sub>5</sub>H<sub>4</sub>P-*t*-Bu<sub>2</sub>]<sub>2</sub>Fe (4.5 mg, 0.01 mmol) in CH<sub>3</sub>CN (2 ml) was stirred for 0.5 h at r.t. Then Cs<sub>2</sub>CO<sub>3</sub> (380 mg, 1.2 mmol), 4-chloro-acetophenone (77 mg, 0.5 mmol), phenylboronic acid (78 mg, 0.65 mmol) and H<sub>2</sub>O (2 ml) were added. Kept

the suspension on stirring for 24 h at 70 °C under pressure of N<sub>2</sub>. Following procedure is the same as ligand-free system above.

Crystal structure analyses. Crystal of **1** was mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector, using Mo K $\alpha$  radiation ( $\lambda$  0.71073 Å). The data was corrected for Lorentz and polarisation effect with the SMART suite of programs [14] and for absorption effects with SADABS [15]. Structure solution and refinement were carried out with the SHELXTL suite of programs [16]. The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. The data collection and processing parameters are given in Table 7.

#### 5. Supplementary material

CCDC 659666 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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