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Pyrazole-tethered phosphine ligands for Pd(0): useful catalysts for Stille, Kumada and Hiyama cross-coupling reactions

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ABSTRACT

Combination of 3,5-dimethyl-1-(2-(diphenylphosphino)phenyl)-1*H*-pyrazole, **A**, and 3-*tert*-butyl-5-methyl-1-(2-(diphenylphosphino)phenyl)-1*H*-pyrazole, **B**, with $Pd_2(dba)_3$ furnished excellent catalysts for Stille, Kumada and Hiyama cross-coupling reactions. Effects of solvents, bases and ligand/palladium ratio on efficiency of coupling reactions were studied. Molecular structures of palladium(II) complexes of **A** and **B** determined by single-crystal X-ray diffraction method revealed a close similarity of ligand arrangement around the metal centre.

1. Introduction

Ligand assisted palladium catalyzed cross-coupling reactions are among the most frequently employed methods of C–C bond formation in organic synthesis.[1] They have been applied to the synthesis of complex natural products, supramolecular architecture and processable materials such as conducting polymers, molecular wires and liquid crystals.[1b,2] The most common palladium precursors used for coupling reactions such as Kumada,[3] Negishi,[4] Stille,[5,17a] Suzuki,[6] Sonogashira,[7] Hiyama[8] and other related reactions,[9,10] are $PdCl_2$, $Pd(OAc)_2$, $Pd_2(dba)_3$ etc., which are commonly stabilized as phosphine complexes. The donor property of phosphorus in such ligands has been fine tuned to provide highly reactive complexes that can readily activate relatively inert aryl chlorides[11] and alkyl halides to widen the scope of coupling reactions.

We earlier demonstrated that pyrazolyl-based phosphine ligands (**A** and **B**) (Fig. 1) are useful in Suzuki reaction[12] and amination[12b] of aryl bromides and electron deficient aryl chlorides. In this paper, we establish that these pyrazolyl tethered phosphine ligands (**A** and **B**) also provide highly active catalysts for Stille, Kumada and Hiyama cross-coupling reactions. In addition, we undertook the synthesis and crystal structural determination of palladium complexes derived from ligand **A** (complex **C**) and ligand **B** (complex **D**) to understand the reason behind the reactivity difference between them.

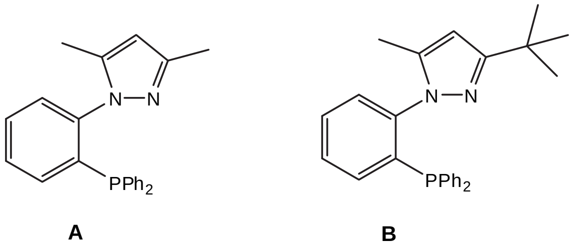

Figure 1. Ligands **A** and **B**.

2. Results and discussion

Ligands **A** and **B** were synthesized following reported procedure[12a] and their effectiveness in catalysis in Stille, Kumada and Hiyama coupling reactions were compared.

2.1. Application of ligand A and B in palladium-catalyzed Stille cross-coupling reaction

The palladium-catalyzed Stille cross-coupling of aryl halides (or halide equivalents) with organotin reagents has found wide application in natural product synthesis,[13] carbohydrate chemistry[14] and biological research.[15] The popularity is due, in part, to the ease of handling of organotin reagents and their excellent functional group tolerance. Generally, palladium catalysts with various

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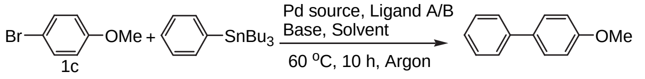
phosphine ligands provide excellent yields and high efficiency.[2c,11a,16,17]

It is known that the performance of a palladium catalyzed reaction is dependent on several factors, e.g., source of palladium, ligand, base, solvent, temperature, etc.[18] We employed the reaction of 4-bromoanisole (**1c**) and phenyltributyltin in presence of 1 mol % of $Pd_2(dba)_3$ and ligand (2 mol %) under argon atmosphere at 60 °C to screen the bases and solvents (Table 1).

Table 1

Palladium-catalyzed Stille cross-coupling reaction of 4-bromoanisole (**1c**) with phenyltributyltin[a]



Entry	Pd/ligand	Pd precursor	Ligand	Base	Solvent	Yield[b] (%)
1	1:1	$Pd_2(dba)_3$	**A**	CsF	Toluene	86
2	1:1	$Pd_2(dba)_3$	**B**	CsF	Toluene	90
3	1:1	$Pd(OAc)_2$	**B**	CsF	Toluene	69
4	1:1	$Pd_2(dba)_3$	**B**	Cs_2CO_3	Toluene	49
5	1:1	$Pd_2(dba)_3$	**B**	K_3PO_4	Toluene	50
6	1:1	$Pd_2(dba)_3$	**B**	CsF	1,4-Dioxan	70
7	1:1	$Pd_2(dba)_3$	**B**	CsF	THF	55
8	1:2	$Pd_2(dba)_3$	**B**	CsF	Toluene	71

[a] 4-bromoanisole (1 mmol), phenyltributyltin (1.2 mmol), $Pd_2(dba)_3$ (1 mol %) or $Pd(OAc)_2$ (2 mol %), ligand **A** or **B** (2 or 4 mol %), base (3 mmol), solvent (3 mL), 60 °C, 10 h.

[b] Isolated yield after flash chromatography (average of two runs).

The results of Table 1 show that ligand **B** is more effective than ligand **A** (entries 1 and 2). Hence ligand **B** was used for subsequent runs. Toluene is the best choice of solvent (better than 1,4-dioxan and THF—entries 2, 6 and 7). Since success of the coupling reaction often depends on the base used,[19] a number of bases were screened. Among all the bases, CsF was found to be the most effective while the reaction was run in toluene (entry 2). The other bases such as Cs_2CO_3 and K_3PO_4, were less effective (entries 4 and 5). It was also found that reaction with $Pd_2(dba)_3$ gave better yields than reactions that used $Pd(OAc)_2$ (see entries 2 and 3). The yield was best when the ratio of ligand/Pd was 1:1 (compare entry 2 with entry 8).

The effect of various aryl bromides bearing electron-donating and electron-withdrawing groups with phenyltributyltin (Table 2: entries 1–20), 2-(tributylstannyl)pyridine (entry 24) and tributyl (vinyl)tin (Table 2: entries 25–28) in presence of 1 mol % of $Pd_2(dba)_3$, 2 mol % of ligand **A** or **B** and 3 equiv of CsF in toluene was investigated. As noted in Table 1, entries in Table 2 also corroborate that ligand **B** is a better choice of ligand than ligand **A** (entries 1–16, 26 and 27). 4-Substituted aryl bromides afforded good to excellent yield of the desired products (entries 1–5, 13–15 and 25–27). Even sterically hindered 2-substituted and 2,6-disubstituted aryl bromides gave good yields (entries 7, 8, 9, 11, 12, 17, 18, 19, 20 and 28). Excellent yields were obtained when heteroaryl bromides were used as substrates with phenyltributyltin in presence of ligand **B** (entries 21–23). Reaction of bromobenzene with 2-(tributylstannyl)pyridine gave the desired cross-coupling product with 78% yield (entry 24).

Table 2

Palladium-catalyzed Stille coupling reaction of aryl halides with tributyltin reagents in the presence of ligand **A** and **B**[a]

$$Ar^1\text{—}Br \quad + \quad R^1\text{——}SnBu_3 \xrightarrow[\text{CsF, Toluene, 10 h}]{\text{Ligand } \mathbf{A} \text{ / } \mathbf{B}\text{, } Pd_2(dba)_3} Ar^1\text{——}R^1$$

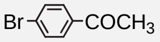
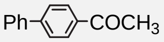
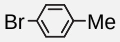
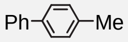
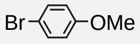
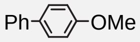
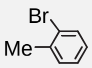
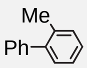
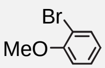
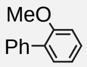
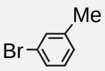
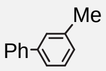
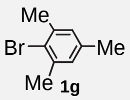
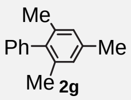
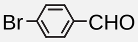
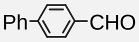
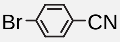
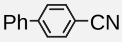
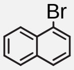
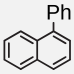
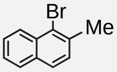
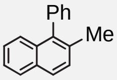
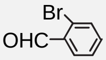
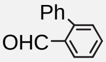
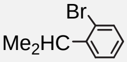
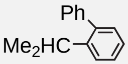
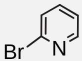
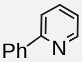
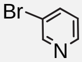
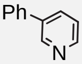
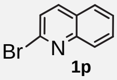
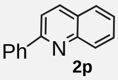
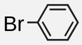
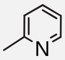
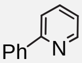
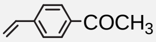
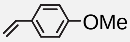
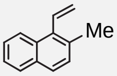
Entry	Ligand	Ar^1–Br	R^1	Product	Yield[b] (%)
1	**A**	 **1a**	–Ph	 **2a**	90
2	**B**	**1a**	–Ph	**2a**	98
3	**A**	 **1b**	–Ph	 **2b**	82
4	**B**	**1b**	–Ph	**2b**	96
5	**A**	 **1c**	–Ph	 **2c**	86
6	**B**	**1c**	–Ph	**2c**	90
7	**A**	 **1d**	–Ph	 **2d**	80
8	**B**	**1d**	–Ph	**2d**	92
9	**B**	 **1e**	–Ph	 **2e**	82
10	**B**	 **1f**	–Ph	 **2f**	96
11	**A**	 **1g**	–Ph	 **2g**	72
12	**B**	**1g**	–Ph	**2g**	80

Table 2 (*continued*)

Entry	Ligand	Ar^1–Br	R^1	Product	Yield[b] (%)
13	**A**	 **1h**	–Ph	 **2h**	85
14	**B**	**1h**	–Ph	**2h**	92
15	**A**	 **1i**	–Ph	 **2i**	90
16	**B**	**1i**	–Ph	**2i**	95
17	**B**	 **1j**	–Ph	 **2j**	90
18	**B**	 **1k**	–Ph	 **2k**	92
19	**B**	 **1l**	–Ph	 **2l**	86
20	**B**	 **1m**	–Ph	 **2m**	88
21	**B**	 **1n**	–Ph	 **2n**	95
22	**B**	 **1o**	–Ph	 **2o**	92
23	**B**	 **1p**	–Ph	 **2p**	88
24	**B**	 **1q**		 **2n**	78
25	**B**	**1a**		 **2a'**	92
26	**A**	**1c**		 **2b'**	82
27	**B**	**1c**		**2b′**	88
28	**B**	**1k**		 **2c'**	95

[a] Aryl bromide (1 mmol), tin compound (1.2 mmol), $Pd_2(dba)_3$ (1 mol %), ligand **A**/**B** (2 mol %), Pd:Ligand **A**/**B** 1:1, CsF (3 mmol), Toluene (3 mL), 60 °C, 10 h.

[b] Isolated yield after flash chromatography (average of two runs).

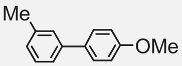
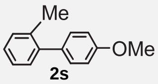
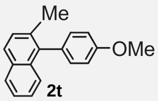
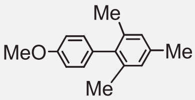
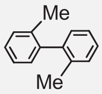
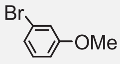
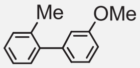
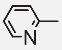
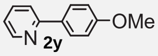
2.2. Application of ligand A and B in palladium catalyzed Kumada cross-coupling reaction

The coupling reaction between an arylmagnesium halide and an aryl halide, often termed Kumada coupling reaction, first reported cross-coupling reaction (early 1970s),[3a,20] is still a popular choice for C–C bond formation after 30 years. The reaction enjoys an obvious advantage: since aryltributyltin and boronic acid derivatives are most commonly prepared from the corresponding Grignard reagents, it reduces an extra step. However, in view of the greater reactivity of the Grignard reagents, the other two methods are often preferred when chemoselectivity is desired.

The catalytic behaviour of ligand **A** and **B** in Kumada cross-coupling reaction was evaluated. The results are summarized in Table 3. In all cases the reactions were performed with $Pd_2(dba)_3$ (1 mol %), ligand (2 mol %), in toluene as solvent at 55 °C. Ligand **B** exhibits a slightly better catalytic activity than ligand **A** (entries 1 and 2). Increased steric hindrance of the substrates is not a deterrent in this reaction. For example, the reactions of 1-bromo-2-methylnaphthalene (**1k**) with 4-OMe/C_6H_4MgBr gave 88% of desired product (**2t**) with ligand **B** (entry 15) and 4-OMeC_6H_4Br (**1c**) with 2,4,6-$Me_3C_6H_2$MgBr furnished 85% of the desired product (**2v**) with ligand **B** (entry 24). Reaction of 3-bromopyridine with phenyl Grignard reagent (entry 9) and 2-pyridyl Grignard reagent with **1c** (entry 25) delivered heterobiaryls **2o** and **2y** in 94 and 86% yields, respectively.

Table 3
Palladium-catalyzed Kumada coupling reaction of various aryl bromides with varying Grignard reagents in the presence of ligand **A** and **B**[a]

$$\mathrm{Ar^1{-}Br} + \mathrm{Ar^2{-}MgBr} \xrightarrow[\text{Toluene, 10 h}]{\text{Ligand } \mathbf{A}/\mathbf{B}\text{, } Pd_2(dba)_3} \mathrm{Ar^1{-}Ar^2}$$

Entry	Ligand	Ar^1–Br	Ar^2	Product	Yield[b] (%)
1	**A**	**1c**	–Ph	**2c**	90
2	**B**	**1c**	–Ph	**2c**	99
3	**A**	**1d**	–Ph	**2d**	87
4	**B**	**1d**	–Ph	**2d**	98
5	**A**	**1a**	–Ph	**2e**	83
6	**B**	**1e**	–Ph	**2e**	90
7	**A**	**1k**	–Ph	**2k**	87
8	**B**	**1k**	–Ph	**2k**	92
9	**B**	**1o**	–Ph	**2o**	94
10	**A**	**1f**	–4OMe–C_6H_4	 **2r**	90
11	**B**	**If**	–4OMe–C_6H_4	**2r**	99
12	**A**	**1d**	–4OMe–C_6H_4	 **2s**	88
13	**B**	**1d**	–4OMe–C_6H_4	**2s**	98
14	**A**	**1k**	–4OMe–C_6H_4	 **2t**	80
15	**B**	**1k**	–4OMe–C_6H_4	**2t**	88
16	**A**	**1g**	–4OMe–C_6H_4	 **2v**	74
17	**B**	**1g**	–4OMe–C_6H_4	**2v**	80
18	**A**	**1d**	–2Me–C_6H_4	 **2w**	86
19	**B**	**1d**	–2Me–C_6H_4	**2w**	98
20	**B**	**1c**	–2Me–C_6H_4	**2s**	93
21	**A**	 **1x**	–2Me–C_6H_4	 **2x**	92
22	**B**	**1x**	–2Me–C_6H_4	**2x**	99
23	**A**	**1c**	–2,4,6-triMe–C_6H_2	**2v**	76
24	**B**	**1c**	–2,4,6-triMe–C_6H_2	**2v**	85
25	**B**	**1c**		 **2y**	86

[a] Aryl bromide (1 mmol), Grignard reagent (2 mmol in THF), Pd2(dba)3 (1 mol %), ligand (2 mol %), Pd/Ligand **A**/**B** 1:1, toluene (2 mL), 55 °C, 10 h.

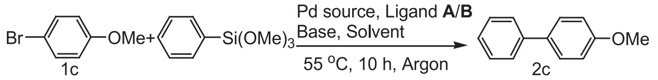
[b] Isolated yield after flash chromatography (average of two runs).

2.3. Application of ligand A and B in palladium-catalyzed Hiyama cross-coupling reaction

Compared to some of the other organometallic reagents that are employed in cross-coupling processes, organosilicon compounds are mild and pose lower toxicity problems. Palladium-catalyzed Hiyama coupling of organosilicon compounds with organic halides and sulfonates, thus, evolved as an important and selective method for producing carbon–carbon bonds.[8,21]

In order to probe the feasibility of a Hiyama cross-coupling of an aryl bromide, a series of screening experiments were carried out. 4-Bromoanisole (**1c**) and trimethoxy(phenyl)silane were used as the model substrates, and Pd_2dba_3 (1 mol %), ligand **B** (2 mol %) were used as the initial catalytic system for a prototypical reaction. The results are summarized in Table 4.

Table 4
Palladium-catalyzed Hiyama cross-coupling reaction of 4-bromoanisole (**1c**) with trimethoxy(phenyl)silane[a]



Entry	Pd/ligand	Pd precursor	Ligand	Base	Solvent	Yield[b] (%)
1	1:1	$Pd_2(dba)_3$	**A**	TBAF	1,4-Dioxan	72
2	1:1	$Pd_2(dba)_3$	**B**	TBAF	1,4-Dioxan	88
3	1:1	$Pd(OAc)_2$	**B**	TBAF	1,4-Dioxan	25
4	1:1	$Pd_2(dba)_3$	**B**	KF	1,4-Dioxan	0
5	1:1	$Pd_2(dba)_3$	**B**	CsF	1,4-Dioxan	0
6	1:1	$Pd_2(dba)_3$	**B**	TBAF	Toluene	52
7	1:1	$Pd_2(dba)_3$	**B**	TBAF	THF	69
8	1:2	$Pd_2(dba)_3$	**B**	TBAF	1,4-Dioxan	68

[a] 4-bromoanisole (1 mmol), phenyltrimethoxysilane, $Pd_2(dba)_3$ (1 mol %), or Pd $(OAc)_2$ (2 mol %), ligand **A** or **B** (2 or 4 mol %), base (3 mmol), solvent (3 mL), 55 °C, 10 h.

[b] Isolated yield after flash chromatography (average of two runs).

Among the commonly used organic solvents we examined, 1,4-dioxan gave the best results (entries 2, 6 and 7). Since the transmetalation of organosilanes proceeds smoothly after the activation by fluoride anion,[22] we initially applied TBAF as the promoter (entry 2). We next tested other fluoride salts. However, neither CsF nor KF provided the desired product (entries 4 and 5). Ligand **B** proved to be a better ligand than ligand **A** in this reaction as well (entries 1 and 2).

The results of Table 4 also demonstrated that $Pd(OAc)_2$ was inferior to $Pd_2(dba)_3$ (entries 2 and 3). Best yield was obtained when the ratio of $Pd_2(dba)_3$/ligand (**B**) was 1:1 (entries 2 and 8).Use of $Pd_2(dba)_3$, (1 mol %), ligand **B** (2 mol %), 3 equiv of TBAF in 1,4-dioxan at 55 °C led to the best results in 10 h.

With this preliminary result in hand, the scope of these Pd-catalyzed Hiyama coupling reactions of aryl bromides were investigated under the optimized conditions, [$Pd_2(dba)_3$ (1 mol %), ligand **A**/**B** (2 mol %), TBAF (3 equiv), 1,4-dioxan, 55 °C], and the results are shown in Table 5. The catalyst/ligand **A**/**B** system were suitable for electronically neutral (entries 3, 4, 7 and 8), electronically deactivated (entries 5, 6, 9 and 10), sterically demanding (entries 11, 12, 17–20) and heteroaryl substrate (entry 21).

2.4. Complexation of ligand A and B with $Pd(CH_3CN)_2Cl_2$

It was consistently observed that catalytic efficiency was dependent on the ligand used, ligand **B** being more effective than ligand **A**. In order to examine whether structural factors were responsible for this difference, it was decided to solve crystal structures of two Pd(II) complexes derived from these ligands, as described below. The corresponding Pd(0) complexes were much more air-sensitive and did not yield stable crystals despite several attempts.

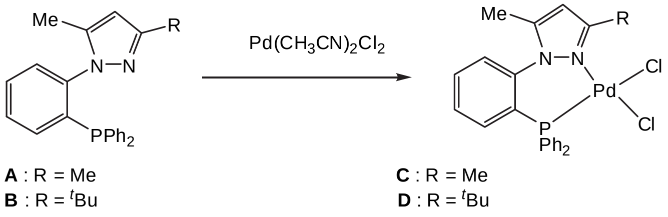
Table 5
Palladium-catalyzed Hiyama coupling reaction of various aryl bromides with trimethoxy(phenyl)silane in the presence of ligand **A** and **B**[a]

$$\mathrm{Ar^1{-}Br} + \mathrm{PhSi(OMe)_3} \xrightarrow[\text{TBAF, 1,4-dioxan, 10 h}]{\text{Ligand }\mathbf{A}/\mathbf{B}\text{, }\mathrm{Pd_2(dba)_3}} \mathrm{Ar^1{-}Ph}$$

Entry	Ligand	Ar^1	Product	Yield[b] (%)
1	**A**	**1a**	**2a**	85
2	**B**	**1a**	**2a**	92
3	**A**	**1b**	**2b**	76
4	**B**	**1b**	**2b**	85
5	**A**	**1c**	**2c**	72
6	**B**	**1c**	**2c**	88
7	**A**	**1d**	**2d**	72
8	**B**	**1d**	**2d**	88
9	**A**	**1e**	**2e**	65
10	**B**	**1e**	**2e**	82
11	**A**	**ig**	**2g**	58
12	**B**	**ig**	**2g**	70
13	**A**	**1h**	**2h**	80
14	**B**	**1h**	**2h**	88
15	**A**	**1i**	**2i**	85
16	**B**	**1i**	**2i**	93
17	**B**	**1j**	**2j**	75
18	**B**	**1k**	**2k**	72
19	**B**	**11**	**21**	76
20	**B**	**1m**	**2m**	72
21	**B**	**1o**	**2o**	88

[a] Aryl bromide (1 mmol), phenyltrimethoxysilane (1.2 mmol), $Pd_2(dba)_3$ (1 mol %), ligand (2 mol %), Pd/Ligand **A**/**B** 1:1, TBAF (3 mmol), 1,4-dioxan (3 mL), 55 °C, 10 h.
[b] Isolated yield after flash chromatography (average of two runs).

The complex (**C**) was synthesized by the addition of stoichiometric amount of ligand **A** to $Pd(CH_3CN)_2Cl_2$, in dichloromethane (Scheme 1).[23] The solution turned intense yellow in about 15 min. After removal of all volatiles under reduced pressure a yellow powder was obtained.



Scheme 1.

Crystallization was performed in dichloromethane/acetonitrile mixture (1:1). In case of complex (**D**), (Scheme 1) chloroform was used as the solvent instead of dichloromethane. An orange coloured precipitate was obtained within 15 min. The precipitate was collected by filtration and crystallized from dichloromethane/acetonitrile (1:1). Poor solubility of these complexes in most common organic solvents did not allow us to obtain their ^{1}H NMR spectra. The identity of these palladium complexes were established by single-crystal X-ray diffraction analysis[24] (See Supplementary data).

A suitable golden-yellow coloured block shaped crystal of complex **C** was grown from acetonitrile/dichloromethane solution by slow evaporation and used for X-ray single crystal diffraction data collection. Complex **C** belonged to centrosymmetric monoclinic space group $P2_1/n$. The asymmetric unit contains one tetracoordinated Pd(II) centre surrounded by two chlorine atoms and ligand **A** coordinated to the metal centre via N and P donor atoms. The metal centre has a distorted square planar geometry [$\angle$Cl(1)–Pd(1)–P(1)=93.12(2)°; $\angle$N(1)–Pd(1)–P(1)=82.09(6)°; $\angle$N(1)–Pd(1)–Cl(2)=91.92(6)°; $\angle$Cl(1)–Pd(1)–Cl(2)=92.93(2)°] (Fig. 2). The complex **C** is stabilized by weak hydrogen bonded interaction via C–H···Cl [C···Cl=3.563(3) Å; $\angle$C–H···Cl=166.00°] leading to the formation of a 1D zig-zag hydrogen bonded network (Fig. 3a and b). Such 1D zig-zag network further interacts with adjacent networks via C–H···Cl interactions involving C–H of methyl group and aromatic C–H with metal coordinated chloride [C···Cl=3.434 Å; $\angle$C–H···Cl=113.17°].

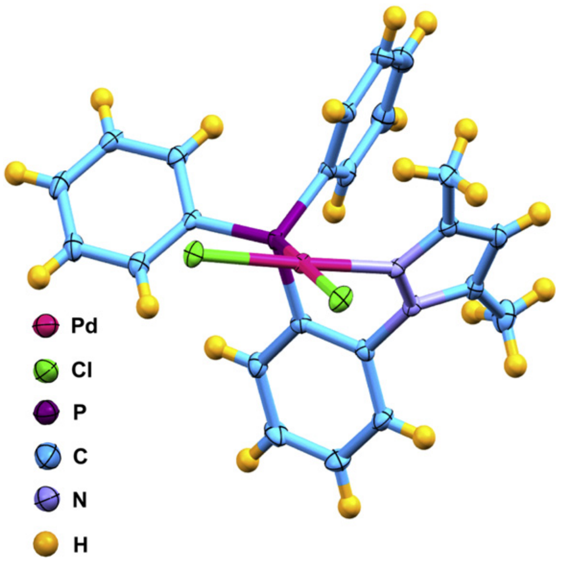


Figure 2. Thermal ellipsoid plot of complex **C** with thermal ellipsoid drawn at 50% probability level.

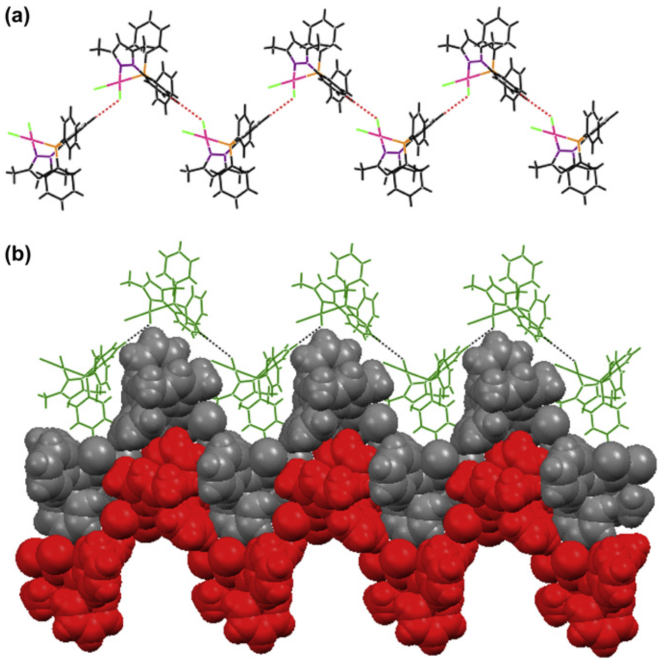


Figure 3. a) 1D zig-zag hydrogen bonded network via C–H···Cl interaction in C and (b) adjacent 1D zig-zag networks shown in different colours first network in capped sticks (green) and others in spacefill model.

A suitable thin plate shaped crystal of **D** was used for X-ray single crystal diffraction data collection. Complex **D** crystallized in centrosymmetric monoclinic space group $P2_1/c$. The asymmetric unit contains one fully occupied Pd(II) with two chlorine atoms and ligand **B** coordinated to the metal centre via N and P donor atoms. The metal centre displays a distorted square planar geometry [$\angle$Cl(1)–Pd(1)–Cl(2)=93.52(2)°; $\angle$Cl(2)–Pd(1)–P(1)=95.18(2)°; $\angle$N(1)–Pd(1)–P(1)=82.24(6)°; $\angle$N(1)–Pd(1)–Cl(1)=91.74(6)°] (Fig. 4).

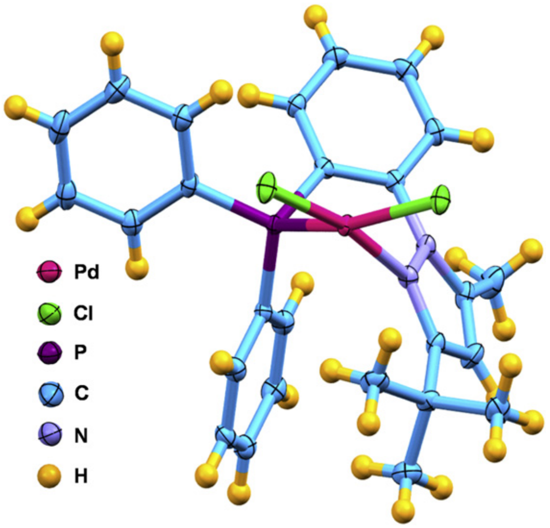


Figure 4. Thermal ellipsoid plot of complex **D** with thermal ellipsoid drawn at 50% probability level.

Weak hydrogen bonding with the metal coordinated chloride and C–H of aromatic ring via C–H···Cl interactions [$\mathrm{C}\cdots\mathrm{Cl}=3.497(3)-3.714(3)$ Å; $\angle \mathrm{C{-}H}\cdots\mathrm{Cl}=138-169^{\circ}$] was observed. It resulted in the formation of a 2D hydrogen bonded microporous network (Fig. 5a and b). The offset packing of such microporous 2D sheets effectively blocked the micropores in the crystal structure (Fig. 6).

The crystal structures thus reveal considerable similarity in terms of geometry at the metal centre and orientation of the groups for the two complexes, **C** and **D**. There is almost no distortion in Cl(1)–Pd–Cl(2) or N–Pd–P angles. The only difference is in the distance between the metal centre and the carbon of the nearest methyl group. In complex **D**, the methyl carbon of the *tert*-butyl group is closer to the metal centre (3.065 Å) than the pyrazole 3-methyl group in complex **C** (3.421 Å). This would imply that the palladium centre in complex **D** is better shielded by the 3-*tert*-butyl group while the palladium metal in complex **C** stands more exposed.

Since distorted square planar arrangement is also expected in the Pd(0) complex, that is, catalytically active, we believe the structural factors revealed in these crystal structures are relevant for the Pd(0) intermediate as well. In that case, the observed difference is reactivity between complexes of these two ligands might only have a steric origin. A sterically demanding ligand environment often accelerates the reductive elimination step, which might account for the observed increase in product yield in comparable reaction time.[25]

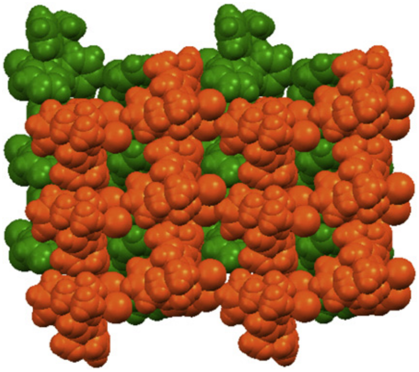


Figure 6. Both adjacent hydrogen bonded layers in spacefill form.

The complex **D** was tested as catalyst for Stille coupling between 4-bromoanisole and phenyltributyltin under the standard condition. About 50% of 4-bromoanisole was recovered after 10 h, whereas the yield of product based on consumed starting material was 81%. The combination of $Pd_2(dba)_3$ and the ligand **B**, on the other hand, yielded the same product in 90% yield and no starting material was left at the end of the reaction (entry 6, Table 2). Taken together, these results suggest that the rate of reaction catalyzed by complex **D** was considerably slow, presumably due to slow reduction of Pd(II) to catalytically active Pd(0) species. Yet, a high yield and selectivity based on consumed substrate in this reaction suggest that the catalytic species, albeit generated rather slowly, is as efficient. Palladium(II) acetate undergoes reduction very readily in presence of phosphine, and hence provides active catalyst almost instantly (see Tables 1 and 4).

3. Conclusion

We have described the utility of pyrazole-derived ligands **A** and **B** in several palladium catalyzed cross-coupling reactions involving aryl bromides. The ligand **B** always provided a better yield of products. However, crystal structure determination of two Pd(II) complexes **C** and **D** featuring these ligands did not present any obvious structural difference that would account for the differential reactivity of the two ligands in the catalytic reactions. Nevertheless, these two ligands were found to be generally useful for the coupling reactions studied, and offer a basis for designing related chiral motifs for asymmetric C–C bond forming reactions.

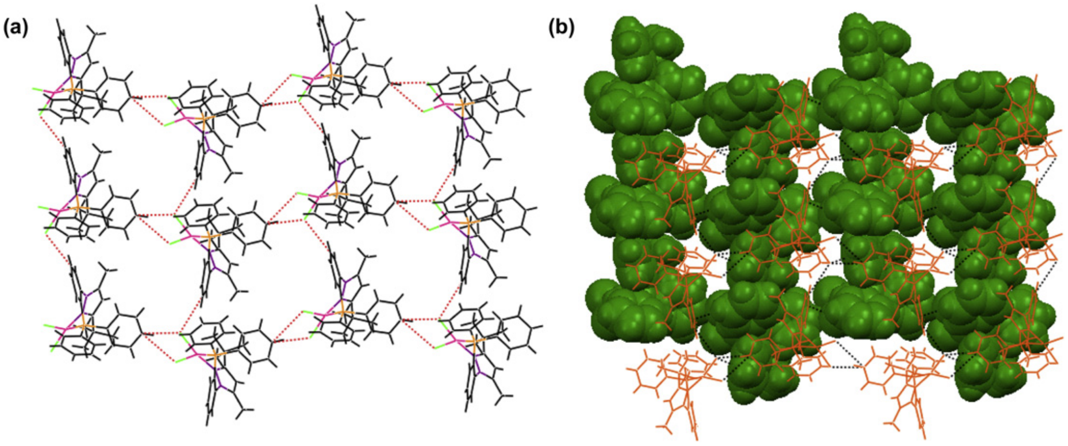


Figure 5. a) 2D hydrogen bonded network via C–H···Cl interaction and (b) offset packing of two adjacent 2D hydrogen bonded networks [adjacent layers in spacefill (green) and capped sticks (orange)].

4. Experimental

4.1. General

All chemicals were purchased as reagent grade from commercial suppliers and used without further purification, unless otherwise noted. 2-(Tributylstannyl)pyridine was prepared following the literature procedure.[26] Reactions were monitored by thin layer chromatography (TLC). All ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz) spectra were recorded as $CDCl_3$ solution and reported in parts per million (δ). Flash Column chromatography was performed with silica gel (230–400 mesh).

4.2. General procedure for palladium catalyzed cross-coupling reaction with ligand A and B

4.2.1. Stille reaction of aryl bromides. A mixture of aryl bromides **1a**–**q** (1 mmol), organotin (1.2 mmol), $Pd_2(dba)_3\cdot CHCl_3$ (1 mol %), ligand **A**/**B** (2 mol %), CsF (3 equiv) and toluene (3 mL) was added in a 2-neck round bottom flask. Then the reaction was stirred at 60 °C under Argon for desired time until complete consumption of starting material as judged by TLC. After the mixture was filtered and evaporated, the residue was purified by flash column chromatography using either petroleum ether or acetone (2–4%)/petroleum ether.

4.2.2. Kumada reaction of aryl bromides. A round bottom flask was charged with aryl bromide (1 mmol), $Pd_2(dba)_3\cdot CHCl_3$ (1 mol %), ligand **A**/**B** (2 mol %), toluene (2 mL), then a THF solution of ArMgBr (2 mmol) was added dropwise at room temperature with stirring. The reaction mixture was stirred at 55 °C for the specified period of time. After the mixture had been cooled to room temperature, the reaction was quenched with water. The aqueous phase was extracted with CH_2Cl_2 and the combined organic layers were dried with Na_2SO_4. The Na_2SO_4 was removed by filtration and the filtrate was concentrated, the residue was purified by flash column chromatography using either petroleum ether or acetone (2–8%)/petroleum ether.

4.2.3. Hiyama reaction of aryl bromides. A mixture of aryl bromides (1 mmol), trimethoxy(phenyl)silane (1.2 mmol), $Pd_2(dba)_3.CHCl_3$ (1 mol %), ligand **A**/**B** (2 mol %), TBAF (3 equiv) and 1,4-dioxan (3 mL) was added in a 2-neck round bottom flask. Then the reaction was stirred at 55 °C under Argon for desired time until complete consumption of starting material as judged by TLC. After the mixture was filtered and evaporated, the residue was purified by flash column chromatography using either petroleum ether or acetone (2–4%)/petroleum ether.

4.3. Synthesis of complex C

A solution of **A** (71 mg, 0.20 mmol) and $PdCl_2(CH_3CN)_2$ (51 mg, 0.20 mmol) in dichloromethane (4 mL) was stirred for 15 min at room temperature, resulting a yellow colour solution. All volatiles were evaporated under reduced pressure and the residue was recrystallized from dichloromethane/acetonitrile solvent mixture.

4.4. Synthesis of complex D

A solution of **B** (80 mg, 0.20 mmol) and $PdCl_2(CH_3CN)_2$ (51 mg, 0.20 mmol) in chloroform (3 mL) was stirred at room temperature, resulting in a yellowish-orange coloured precipitate within 15 min. All volatiles were evaporated under reduced pressure and the residue was recrystallized from dichloromethane/acetonitrile solvent mixture.

Acknowledgements

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Supplementary data

Supplementary data (contains copies of ^{1}H and ^{13}C NMR spectra of all products listed in the tables) associated with this article provided as a separate file. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 755275 and 755274 for **C** and **D**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.05.026. These data include MOL files and InChiKeys of the most important compounds described in this article.

References and notes

1. General reviews, see: (a) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174; (b) Corbet, J.-P.; Mignani, G. *Chem. Rev.* **2006**, *106*, 2651; (c) *Cross-Coupling Reactions: A Practical Guide in Topics in Current Chemistry*; Houk, K. N., Sessler, H., Lehn, J.-M., Ley, S. V., de Meijere, A., Schreiber, S. L., Thiem, J., Trost, B. M., Vögtle, F., Yamamoto, H., Eds.; Springer: Heidelberg, 2002; Vol. 219; (d) Hegedus, L. S. In *Organometallics in Organic Synthesis*; Schlosser, M., Ed.; Wiley: New York, NY, 1994; p 383; (e) *Palladium Reagents and Catalysts: Innovations in Organic Synthesis*; Fuji, J., Ed.; Wiley: Chichester, UK, 1995; (f) Geissler, H. In *Transition Metals for Organic Synthesis*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 1, pp 158–193; (g) *Metal-Catalyzed Cross-coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, Germany, 1998; (h) *Palladium in Heterocyclic Chemistry: A Guide for the Synthetic Chemist*; Li, J. J., Gribble, G. W., Eds.; Pergamon: Amsterdam, 2000.
2. (a) Yin, L.; Liebscher, J. *Chem. Rev.* **2007**, *107*, 133; (b) Phan, N. T. S.; Van Der Sluys, M.; Jones, C. W. *Adv. Synth. Catal.* **2006**, *348*, 609; (c) Hassan, J.; Sévignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359; (d) Belardi, J. K.; Micalizio, G. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 4005; (e) Jia, Y.; Bois-Choussy, M.; Zhu, J. *Angew. Chem., Int. Ed.* **2008**, *47*, 4167; (f) Burlison, J. A.; Neckers, L.; Smith, A. B.; Maxwell, A.; Blagg, B. S. J. *J. Am. Chem. Soc.* **2006**, *128*, 15529; (g) Nicolaou, K. C.; Li, H.; Boddy, C. N. C.; Ramanjulu, J. M.; Yue, T. Y.; Natarajan, S.; Chu, X.; Bräse, J. S.; Rübsam, F. *Chem.—Eur. J.* **1999**, *5*, 2584; (h) Stanforth, S. P. *Tetrahedron* **1998**, *54*, 263.
3. (a) Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374; (b) Phan, N. T. S.; Brown, D. H.; Styring, P. *Green Chem.* **2004**, *6*, 526.
4. (a) Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340; (b) Negishi, E.; Anastasia, L. *Chem. Rev.* **2003**, *103*, 1979.
5. (a) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 3636; (b) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508; (c) Garcia-Martinez, J. C.; Lezutekong, R.; Crooks, R. M. *J. Am. Chem. Soc.* **2005**, *127*, 5097.
6. (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457; (b) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147; (c) Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550; (d) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020; (e) Kotha, S.; Lahiri, K.; Kashinath, D. *Tetrahedron* **2002**, *58*, 9633; (f) Navarro, O.; Oonishi, Y.; Kelly, R. A.; Stevens, E. E.; Briel, O.; Nolan, S. P. *J. Organomet. Chem.* **2004**, *689*, 3722; (g) Mukherjee, A.; Sarkar, A. *Tetrahedron Lett.* **2005**, *46*, 15; (h) Srimani, D.; Sarkar, A. *Tetrahedron Lett.* **2008**, *49*, 6304; (i) Patil, S. A.; Weng, C.-M.; Huang, P.-C.; Hong, F.-E. *Tetrahedron* **2009**, *65*, 2889.
7. (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467; (b) Sonogashira, K. *J. Organomet. Chem.* **2002**, *653*, 46; (c) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3066.
8. For a review of the Hiyama reaction, see: (a) Hiyama, T. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: New York, NY, 1998; Chapter 10; (b) Hiyama, T. *J. Organomet. Chem.* **2002**, *653*, 58; (c) Denmark, S. E.; Baird, J. D. *Chem.—Eur. J.* **2006**, *12*, 4954; (d) Strotman, N. A.; Sommer, S.; Fu, G. C. *Angew. Chem., Int. Ed.* **2007**, *46*, 3556.
9. Hartwig/Buchwald amination; (a) Guram, A. S.; Rennels, R. A.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **1995**, *34*, 1348; (b) Louie, J.; Hartwig, J. F. *Tetrahedron Lett.* **1995**, *36*, 3609; (c) Wolfe, J. P.; Wagaw, S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 7215; (d) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7217; (e) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 8232; (f) Hamann, B. C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1998**, *120*, 7369; (g) Hartwig, J. F.; Kawatsura, M.; Hauck, S. I.; Shaughnessy, K. H.; Alcazar-Roman, L. M. *J. Org. Chem.* **1999**, *64*,

5575; (h) Wolfe, J. P.; Buchwald, S. L. *Angew.Chem., Int. Ed.* **1999**, *38*, 2413; (i) Yin, J.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 6043; (j) Schlummer, B.; Scholz, U. *Synth. Catal.* **2004**, *346*, 1599.

10. Hartwig/Buchwald arylation of carbonyl compounds; (a) Palucki, M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 11108; (b) Hamann, B. C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 12382; (c) Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 1473; (d) Lee, S.; Hartwig, J. F. *J. Org. Chem.* **2001**, *66*, 3402; (e) Lee, S.; Beare, N. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 8410; (f) Jörgensen, M.; Lee, S.; Liu, X.; Wolkowski, J. P.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 12557; (g) Beare, N. A.; Hartwig, J. F. *J. Org. Chem.* **2002**, *67*, 541; (h) Culkin, D. A.; Hartwig, J. F. *Acc. Chem. Res.* **2003**, *36*, 234; (i) Hama, T.; Culkin, D. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 4976.
11. (a) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176; (b) Bedford, R. B. *Chem. Commun.* **2003**, 1787; (c) Miura, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2201; (d) Botella, L.; Nàjera, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 179; (e) Colacot, T. J.; Shea, H. A. *Org. Lett.* **2004**, *6*, 3731; (f) Böhm, V. P.; Weskamp, W. T.; Gstöttmayer, C. W. K.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 1602; (g) Nabera, J. R.; Buchwald, S. L. *Adv. Synth. Catal.* **2008**, *350*, 957 and references cited therein; (h) Yu, S.-B.; Hua, X.-P.; Huang, J.-D.; Wang, D.-Y.; Duan, Z.-C.; Zheng, Z. *Tetrahedron Lett.* **2008**, *49*, 1253 and references cited therein; (i) Gouda, K.-I.; Hagiwara, E.; Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1996**, *61*, 7232.
12. (a) Mukherjee, A.; Sarkar, A. *Tetrahedron Lett.* **2004**, *45*, 9525; (b) Mukherjee, A.; Sarkar, A. *Arkivo* **2003**, 87.
13. (a) Nicolaou, K. C.; Li, Y.; Sugita, K.; Monenschein, H.; Guntupali, P.; Mitchell, H. J.; Fylaktakidou, K. C.; Vourloumis, D.; Giannakakou, P.; O'Brate, A. *J. Am. Chem. Soc.* **2003**, *125*, 15443; (b) Kadota, I.; Takamura, H.; Sato, K.; Ohno, A.; Matsuda, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **2003**, *125*, 46; (c) Lin, S.-Y.; Chen, C.-L.; Lee, Y.-J. *J. Org. Chem.* **2003**, *68*, 2968; (d) Boger, D. L.; Ichikawa, S.; Jing, H. *J. Am. Chem. Soc.* **2000**, *122*, 12169; (e) Jensen, M. S.; Yang, C.; Hsiao, Y.; Rivera, N.; Wells, K. M.; Chung, J. Y. L.; Yasuda, N.; Hughes, D. L.; Reider, P. J. *Org. Lett.* **2000**, *2*, 1081.
14. Kuribayashi, T.; Gohya, S.; Mizuno, Y.; Satoh, S. J. *Carbohyd. Chem.* **1999**, *18*, 383.
15. Nicolaou, K. C.; King, N. P.; Finlay, M. R. V.; He, Y.; Roschangar, F.; Vourloumis, D.; Vallberg, H.; Sarabia, F.; Ninkovic, S.; Hepworth, D. *Bioorg. Med. Chem.* **1999**, *7*, 665.
16. For reviews, see: (a) See Ref. 1g; (b) Shirakawa, E.; Hiyama, T. *J. Organomet. Chem.* **1999**, *576*, 169; (c) Miyaura, N. *Cross-Coupling Reaction*; Springer: Berlin, 2002; (d) Hegedus, L. S. In *Oranometallics in Synthesis*; Schlosser, M., Ed.; J. Wiley & Sons: Chichester, UK, 2002; p 1123; (e) *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; Wiley-Interscience: New York, NY, 2002; (f) Espinet, P.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 4704.
17. For recent representative papers on phosphine/palladium catalysts, see: (a) Litter, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **1999**, *38*, 2411; (b) Grasa, G. A.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 119; (c) Litter, A. F.; Schwarz, L.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 6343 and references cited therein; (d) Kim, Y. M.; Yu, S. *J. Am. Chem. Soc.* **2003**, *125*, 1696; (e) Menzel, K.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 3718; (f) Kim, W.-S.; Kim, H.-J.; Cho, C.-G. *J. Am. Chem. Soc.* **2003**, *125*, 14288; (g) Dubbaka, S. R.; Vogel, P. *J. Am. Chem. Soc.* **2003**, *125*, 15292; (h) Tang, H.; Menzel, K.; Fu, G. C. *Angew. Chem., Int. Ed.* **2003**, *42*, 5079; (i) Wolf, C.; Lerebours, R. *J. Org. Chem.* **2003**, *68*, 7077; (j) Wolf, C.; Lerebours, R. *J. Org. Chem.* **2003**, *68*, 7551; (k) Mee, S. P. H.; Lee, V.; Baldwin, J. E. *Angew. Chem., Int. Ed.* **2004**, *43*, 1132; (l) Su, W.; Urgaonkar, S.; Verkade, J. G. *Org. Lett.* **2004**, *6*, 1421; (m) Mazzola, R. D., Jr.; Giese, S.; Benson, C.; West, F. G. *J. Org. Chem.* **2004**, *69*, 220; (n) Högenauer, K. *Synlett* **2001**, 878; (o) Scrivanti, A.; Matteoli, U.; Beghetto, V.; Antonaroli, S.; Crociani, B. *Tetrahedron* **2002**, *58*, 6881; (p) Kim, N.; Kwon, M. S.; Park, C. M.; Park, J. *Tetrahedron Lett.* **2004**, *45*, 7057.
18. (a) Goldman, E. R.; Medintz, I. L.; Whitley, J. L.; Hayhurst, A.; Clapp, A. R.; Uyeda, H. T.; Deschamps, J. R.; Lassman, M. E.; Mattoussi, H. *J. Am. Chem. Soc.* **2005**, *127*, 6744; (b) Braga, A. A. C.; Morgon, N. H.; Ujaque, G.; Maseras, F. *J. Am. Chem. Soc.* **2005**, *127*, 9298.
19. (a) Miyaura, N.; Yamada, K.; Suginome, H.; Suzuki, A. *J. Am. Chem. Soc.* **1985**, *107*, 972; (b) Grasa, G. A.; Hillier, A. C.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 1077; (c) Dubbaka, S. R.; Vogel, P. *Org. Lett.* **2004**, *6*, 95.
20. (a) See Ref.1g; (b) *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; de Meijere, A., Diederich, F., Eds.; Wiley-VCH:: Weinheim, Germany, 2004; Vols. 1 and 2; (c) Corriu, R. J. P.; Masse, J. P. *J. Chem. Soc., Chem. Commun.* **1972**, 144; (d) Schröter, S.; Stock, C.; Bach, T. *Tetrahedron* **2005**, *61*, 2245.
21. For some recent developments in Hiyama cross-coupling chemistry, see: (a) Denmark, S. E.; Sweis, R. F. *Acc. Chem. Res.* **2002**, *35*, 835; (b) Itami, K.; Nokami, T.; Yoshida, J.-I. *J. Am. Chem. Soc.* **2001**, *123*, 5600 and references therein;; (c) Lee, J.-Y.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 5616; (d) Clarke, M. L. *Adv. Synth. Catal.* **2005**, *347*, 303; (e) Seganish, W. M.; Handy, C. J.; DeShong, P. *J. Org. Chem.* **2005**, *70*, 8948; (f) Alacid, E.; Nàjera, C. *Adv. Synth. Catal.* **2006**, *348*, 945; (g) Denmark, S. E.; Butler, C. R. *Org. Lett.* **2006**, *8*, 63; (h) Gordillo, À.; de Jesús, E.; López-Mardomingo, C. *Org. Lett.* **2006**, *8*, 3517; (i) Napier, S.; Marcuccio, S. M.; Tye, H.; Whittaker, M. *Tetrahedron Lett.* **2008**, *49*, 3939; (j) Napier, S.; Marcuccio, S. M.; Tye, H.; Whittaker, M. *Tetrahedron Lett.* **2008**, *49*, 6314; (k) Nakao, Y.; Oda, T.; Sahoo, A. K.; Hiyama, T. *J. Organomet. Chem.* **2003**, *687*, 570; (l) Sahoo, A. K.; Oda, T.; Nakao, Y.; Hiyama, T. *Adv. Synth. Catal.* **2004**, *346*, 1715; (m) Shibata, K.; Miyazawa, K.; Goto, Y. *Chem. Commun.* **1997**, 1309; (n) Hirabayashi, K.; Mori, A.; Kawashima, J.; Suguro, M.; Nishihara, Y.; Hiyama, T. *J. Org. Chem.* **2000**, *65*, 5342; (o) Riggleman, S.; DeShong, P. *J. Org. Chem.* **2003**, *68*, 8106; (p) Mowery, M. E.; DeShong, P. *J. Org. Chem.* **1999**, *64*, 1684; (q) Lee, H. M.; Nolan, S. P. *Org. Lett.* **2000**, *2*, 2053; (r) Denmark, S. E.; Ober, M. H. *Org. Lett.* **2003**, *5*, 1357; (s) Mowery, M. E.; DeShong, P. *Org. Lett.* **1999**, *1*, 2137; (t) Seganish, W. M.; DeShong, P. *J. Org. Chem.* **2004**, *69*, 1137; (u) Nakao, Y.; Imanaka, H.; Sahoo, A. K.; Yada, A.; Hiyama, T. *J. Am. Chem. Soc.* **2005**, *127*, 6952; (v) Wolf, C.; Lerebours, R.; Tanzini, E. H. *Synthesis* **2003**, 2069; (w) Koike, T.; Mori, A. *Synlett* **2003**, 1850.
22. Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 918.
23. Grossman, O.; Azerraf, C.; Gelman, D. *Organometallics* **2006**, *25*, 375.
24. X-ray quality crystals of Complex **C** and **D** were obtained by the slow evaporation acetonitrile solution at room temperature. X-ray single crystal data were collected using Mo Kα (λ=0.7107 Å) radiation on a BRUKER APEX II diffractometer equipped with CCD area detector. Data collection, data reduction and structure solution/refinement were carried out using the software package of SMART APEX. Both the structures were solved by direct methods and refined in a routine manner. In both cases, non-hydrogen atoms were treated anisotropically and the hydrogen atoms were geometrically fixed at their idealized positions. Crystallographic data for the structural analysis of compounds reported herein have been deposited at the Cambridge Crystallographic Data Centre, CCDC nos. 755275 and 755274 for Complexes **C** and **D**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1233 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).
25. The authors thank one of the reviewers for drawing their attention to this possibility.
26. Bianchini, C.; Gatteschi, D.; Giambastiani, G.; Rios, I. G.; Ienco, A.; Laschi, F.; Mealli, C.; Meli, A.; Sorace, L.; Toti, A.; Vizza, F. *Organometallics* **2007**, *26*, 726.