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Iminophosphine–palladium(0) complexes as catalysts for the Stille reaction

A. Scrivanti,[a,*] U. Matteoli,[a] V. Beghetto,[a] S. Antonaroli[b] and B. Crociani[b]

[a]*Dipartimento di Chimica, Università 'Cà Foscari' di Venezia, Calle Larga S. Marta 2137, Dorsoduro, 30123 Venezia, Italy*
[b]*Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma 'Tor Vergata', Via della Ricerca Scientifica, 00133 Rome, Italy*

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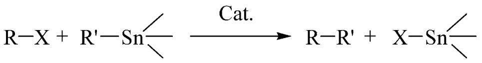
Abstract—The cross-coupling of iodobenzene with tributylphenylethynylstannane or tributylvinylstannane is efficiently catalysed by iminophosphine–palladium(0)–olefin complexes of the type [Pd(η^2-dmf)(P-N)] (dmf, dimethylfumarate; P-N, 1-(PPh_2)-C_6H_4-2-C=NR (R=alkyl, aryl)). The catalytic activity depends on the R substituent of the imino group: the highest reaction rates are obtained using aryl-substituted iminophosphines. Equivalent catalytic systems can be obtained using a palladium source such as $Pd(OAc)_2$ or $Pd(dba)_2$ (dibenzylideneacetone, dba) in combination with the iminophosphine ligands. In the coupling of iodobenzene with tributylphenylethynylstannane, the highest reaction rates are obtained using an iminophosphine/palladium molar ratio of 2:1, while in the vinylstannane–iodobenzene coupling the best P-N/Pd ratio is 1:1.

1. Introduction

The palladium catalysed cross coupling of organostannanes with alkyl or aryl halides (Stille reaction, Eq. (1)) is one of the most important reactions leading to the formation of a new carbon–carbon bond.[1–5]



(1)

Many facets make this reaction a very powerful tool for fine chemicals synthesis. It is particularly important to mention (i) its versatility (a broad range of R and R′ groups can be coupled), (ii) the fact that the R′ group, on the organometallic reagent, can tolerate the presence of a wide variety of functional groups and (iii) its high chemo and stereoselectivity.

Moreover, the use of organostannanes is not a limiting factor owing to their prompt availability.[6]

Usually, the reaction is carried out in the presence of 1–2% of a palladium catalyst. A variety of palladium(II) or palladium(0) phosphine complexes with neutral ligands have been successfully used as catalyst precursors.[1–5] The catalyst efficiency is determined by the nature of the ligand. Triphenylphosphine was the ligand commonly used until it was shown by Farina that enhanced reaction rates can be achieved employing tri(2-furyl)phosphine or triphenylarsine.[7] The rate enhancing effect of a number of promoter such as CuI,[8] CuCl,[9] and diethylamine[10] has also been reported.

More recently, two major breakthroughs have been reported by Shirakawa,[11–13] who claimed that allyl complex $[PdCl(\eta^3\text{-}C_3H_5)]_2$ in combination with the iminophosphine 1-(PPh_2)-C_6H_4-2-C=NCH_2CH_2Ph is even more efficient than the Farina system, and by Fu,[14] who found that the coupling reaction can be suitably carried out even with X=Cl in the presence of P^tBu_3. Finally, it is worth noting that very recently systems catalytic in tin have also been disclosed.[15,16]

Owing to our interest in the chemistry and catalytic activity of iminophosphine–palladium(0) complexes of the type [Pd(η^2-ol)(P-N)] (ol, activated olefin; P-N, 1-(PPh_2)-C_6H_4-2-C=NR),[17,18] the high reaction rates obtained by Shirakawa appeared to us very interesting and prompted us to investigate the catalytic behaviour of the zerovalent complexes [Pd(η^2-ol)(P-N)] shown in Fig. 1. In polar and coordinating solvents or in the presence of free iminophosphine, these compounds containing an alkene of moderate π-accepting properties such as dimethylfumarate may undergo olefin dissociation forming highly reactive palladium(0) intermediates.[19] A wide variety of iminophosphine ligands have been used in order to highlight the influence of the imino substituent R on the reaction rate.

2. Results and discussion

Complexes **1a–4a** were synthesised as described in the literature.[17] The new ligands **5** and **6** were prepared by

Keywords: palladium; catalysis; iminophosphine; Stille reaction.

* Corresponding author. Tel.: +39-0412348903; fax: +39-0412348517; e-mail: scrivant@unive.it

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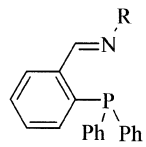
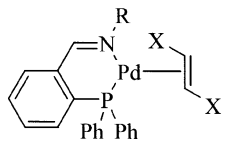


1: R = Me
2: R = CMe_3
3: R = Ph
4: R = 4-MeOPh
5: R = 4-FPh
6: R = 4-CF_3Ph
7: R = CH_2CH_2Ph



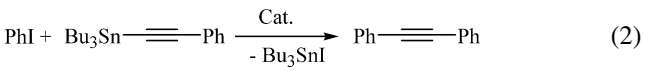
X = $COOCH_3$

1a: R = Me
2a: R = CMe_3
3a: R = Ph
4a: R = 4-MeOPh

Figure 1.

reacting 2-(diphenylphosphino)benzaldehyde[20] with 4-trifluoromethylaniline or 4-fluoroaniline following a well established procedure[17] (see Section 4).

To evaluate the catalytic efficiency of these complexes in the Stille reaction, we chose the coupling of iodobenzene with tributylphenylethynylstannane (Eq. (2)) as a model reaction.



PhI + Bu_3Sn—≡—Ph —(Cat., - Bu_3SnI)→ Ph—≡—Ph (2)

In preliminary investigations, we used the experimental conditions typical for the Stille reaction: equimolecular amounts of the aryl iodide and the organostannane were reacted in THF in the presence of 1 mol% of palladium(0) complex. The product yields after 2 h (see Table 1) indicate that the reaction proceeds at a reasonably good rate and that it is also highly chemoselective, since no side product was detected. Interestingly, the catalytic activity appears to be dependent on both the steric and electronic properties of the R group on the imino nitrogen. In fact, the conversion increases on going from a methyl group to the more sterically demanding *t*-butyl group and when the alkyl substituents are replaced by aryl groups.

The Stille reaction can be carried out in a wide range of solvents.[1] To ascertain the effect of the solvent on the catalytic activity we have carried out a set of isochronous experiments with complex **4a**. The data reported in Table 2 shows an increasing rate in solvents of increasing polarity and donor properties. The rate enhancement obtained with highly boiling solvents such as dimethylsulfoxide or dimethylformamide is of practical interest: in fact their use allows an increase of reaction temperature, making possible the coupling of less reactive substrates able to withstand harsh experimental conditions.

Table 1. Coupling of iodobenzene with tributylphenylethynylstannane: preliminary catalytic data

Run	Catalyst	Stannane/Pd[a]	Yield (%)
1	**1a**	100:1	40
2	**2a**	100:1	60
3	**3a**	100:1	79
4	**4a**	100:1	75

T: 50°C; *t*: 2 h; solvent: THF (5 mL); PhI=PhC≡$CSnBu_3$=1.30 mmol.
[a] Molar ratio.

Table 2. Coupling of iodobenzene with tributylphenylethynylstannane: influence of the solvent

Run	Solvent	Yield (%)
1	Dimethylformamide	91
2	Dimethyl sulfoxide	87
3	Acetonitrile	85
4	Tetrahydrofuran	75
5	Dioxane	68
6	Toluene	65
7	Diglyme	63

T: 50°C; *t*: 2 h; solvent: 5 mL; catalyst: complex **4a**; PhI=PhC≡$CSnBu_3$=1.30 mmol; stannane/catalyst=100:1.

Next, the effect of the ligand/palladium molar ratio on the catalytic activity was investigated. As a matter of fact, the iminophosphines can act as bidentate P,N-chelating ligands, or as monodentate P-ligands,[17] and this flexibility could be advantageous for the catalysis.

The results presented in Table 3 indicate that the addition of 1 equiv. of free ligand to complexes **1a**–**4a** has an indubitable beneficial effect on the reaction rate. On the contrary, the addition of a second equivalent of iminophosphine has very little practical effect. Only in the case of **2a**, the addition of 2 equiv. of free ligand depresses the catalyst activity.

At 2:1 P-N/Pd, total substrate conversion was achieved in 2 h both using **3a** and **4a**: this makes it impossible to fully appreciate the effect of the nature of the aryl group on the catalysis. However, this finding suggests that substrate/complex ratios higher than 100:1 can be conveniently employed with these systems. Accordingly, we have carried out a set of experiments using **3a** at increasingly higher substrate/catalyst ratios.

The data collected in Table 4 show that the coupling can be carried out even at substrate/catalyst ratios as high as 1000:1 in reasonable reaction times. Moreover the data in Table 4 highlights a very intriguing aspect of the catalysis. By comparing the data of runs 5 and 6, it appears that although higher initial reaction rates are achieved working with 2 equiv. of P-N, at longer reaction times the conversion is not much higher than that observed when only 1 equiv. of

Table 3. Coupling of iodobenzene with tributylphenylethynylstannane: effect of the addition of free ligand

Run	Catalyst	Added ligand	P-N/Pd[a]	Yield (%)
1	**1a**	–	1	40
2	**1a**	**1**	2	84
3	**1a**	**1**	3	86
4	**2a**	–	1	60
5	**2a**	**2**	2	80
6	**2a**	**2**	3	57
7	**3a**	–	1	79
8	**3a**	**3**	2	100
9	**3a**	**3**	3	100
10	**4a**	–	1	75
11	**4a**	**4**	2	100
12	**4a**	**4**	3	100

T: 50°C; *t*: 2 h; solvent: THF (5 mL); PhI=PhC≡$CSnBu_3$=1.30 mmol; stannane/catalyst=100:1.
[a] Total ligand/Pd molar ratio.

Table 4. Coupling of iodobenzene with tributylphenylethynylstannane: catalytic activity of **3a**

Run	Catalyst	Added ligand	P-N/Pd[a]	Stannane/Pd[b]	Yield (%) at different times					
					1 h	2 h	3 h	4 h	6 h	24 h
1	**3a**	**3**	2:1	200:1	–	100				
2	**3a**	**3**	3:1	200:1	–	100				
3	**3a**	**3**	2:1	400:1	68	86				
4	**3a**	**3**	3:1	400:1	69	87				
5[c]	**3a**	–	1:1	1000:1	20	28	35	41	51	82
6[c]	**3a**	**3**	2:1	1000:1	34	54	63	68	70	85

T: 50°C; solvent: THF (5 mL); PhI=PhC≡CSnBu$_3$=1.30 mmol.
[a] Total ligand/Pd molar ratio.
[b] Molar ratio.
[c] Solvent: THF (10 mL); PhI=PhC≡CSnBu$_3$=2.70 mmol.

Table 5. Coupling of iodobenzene with tributylphenylethynylstannane: activity of different catalyst precursors

Run	Catalyst	Added ligand[a]	Stannane/Pd[b]	Yield (%)
1	**1a**	**1**	100:1	84
2	Pd(dba)$_2$	**1**	100:1	92
3	Pd(OAc)$_2$	**1**	100:1	86
4	**3a**	**3**	400:1	86
5	Pd(dba)$_2$	**3**	400:1	89
6	Pd(OAc)$_2$	**3**	400:1	88
7[c]	**3a**	**3**	1000:1	54
8[c]	Pd(dba)$_2$	**3**	1000:1	53
9[c]	Pd(OAc)$_2$	**3**	1000:1	55

T: 50°C; *t*: 2 h; solvent: THF (5 mL); PhI=PhC≡CSnBu$_3$=1.30 mmol.
[a] Total ligand/Pd molar ratio=2:1.
[b] Molar ratio.
[c] Solvent: THF (10 mL); PhI=PhC≡CSnBu$_3$=2.70 mmol.

the ligand is used. The slowing down of the reaction rate at high substrate conversions is a quite general feature in Stille's coupling, and it is attributed to poorly understood processes leading to partial decomposition of the catalyst.[7]

Although the synthesis of complexes **1a**–**4a** is not particularly laborious, the possibility to employ some commercially available palladium(0) species as catalyst precursors could add further interest to the excellent results reported here. Thus, we have investigated the activity of the systems prepared by mixing in situ iminophosphines **1**–**7** with some commercially available palladium derivatives such as Pd(dba)$_2$ (dba, dibenzylideneacetone)[20,21] or Pd(OAc)$_2$ widely used as catalyst precursors (Table 5).

According to the data presented in Table 5, the tested systems show a catalytic activity almost identical: the small differences observed appear to be within the experimental error in the determination of the product yield. This similarity is further confirmed by the data obtained at higher substrate/catalyst ratios using different P-N/Pd ratios and reaction times (Table 6). Therefore, it is likely that all three catalytic systems give rise to a unique catalytic species under reaction conditions.

Table 7. Coupling of iodobenzene with tributylphenylethynylstannane: effect of the nature of the ligand

Run	Catalyst	Added ligand	Ligand/Pd[a]	Yield (%) at different times			
				1 h	2 h	4 h	24 h
1	Pd(OAc)$_2$	**1**	2:1	6	11	15	64
2	Pd(OAc)$_2$	**3**	2:1	36	55	69	85
3	Pd(OAc)$_2$	**4**	2:1	34	58	67	93
4	Pd(OAc)$_2$	**5**	2:1	16	26	59	90
5	Pd(OAc)$_2$	**6**	2:1	19	27	51	87
6	Pd(OAc)$_2$	**7**	2:1	3	5	10	69
7	Pd(dba)$_2$	P(fur)$_3$	2:1	44	58	67	80
8	Pd(dba)$_2$	P(fur)$_3$	4:1	49	65	74	81
9	Pd(dba)$_2$	**3**	2:1	38	53	62	82

T: 50°C; solvent: THF (10 mL); PhI=PhC≡CSnBu$_3$=2.70 mmol; stannane/Pd=1000:1.
[a] Total ligand/Pd molar ratio.

Unquestionably, among the systems tested here, Pd(OAc)$_2$ emerges as the most convenient catalyst precursor owing to its commercial availability, its price and shelf durability. Therefore we chose this species to fully investigate the effect of the nature of the iminophosphine ligand (Table 7). The data in Table 7 demonstrates that the highest catalytic efficiency is achieved when the R substituent is an aryl group. Particularly good results are obtained with R=Ph and 4-MeOPh (runs 2 and 3). With aryl groups bearing electron-withdrawing *para* substituents, such as –F or –CF$_3$, the initial reaction rates are somewhat lower (runs 4 and 5), however the final product yields are similar to those obtained with **3** and **4**. On the contrary, when R is an

Table 6. Coupling of iodobenzene with tributylphenylethynylstannane at various P-N/Pd ratios and reaction times

Run	Catalyst	Added ligand	P-N/Pd[a]	Yield (%) at different times					
				1 h	2 h	3 h	4 h	6 h	24 h
1	**3a**	**3**	1:1	20	28	35	41	51	82
2	Pd(OAc)$_2$	**3**	1:1	21	29	37	41	51	83
3	**3a**	**3**	2:1	34	54	63	68	70	85
4	Pd(OAc)$_2$	**3**	2:1	36	55	63	69	71	85

T: 50°C; solvent: THF (10 mL); PhI=PhC≡CSnBu$_3$=2.70 mmol; stannane/Pd=1000:1.
[a] Total ligand/Pd molar ratio.

Table 8. Coupling of iodobenzene with tributylphenylethynylstannane: relative reactivity of halobenzenes

Run	Catalyst	Aryl halide	Yield (%) at different times		
			2 h	4 h	24 h
1	$Pd(OAc)_2$/**3**	PhI	100		
2	$Pd(OAc)_2$/**3**	PhBr	30	40	78
3	$Pd(OAc)_2$/**3**	PhCl	0	0	3

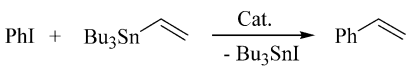
T: 90°C; *t*: 24 h; solvent: dioxane (5 mL); PhX=PhC≡CSnBu$_3$=1.30 mmol; stannane/Pd=200:1; ligand/Pd=2:1.

alkyl group, such as Me or CH_2CH_2Ph, much lower catalytic activities are observed (runs 1 and 6).

To further assess the catalytic efficiency of the systems with iminophosphines **3**–**7**, their activity was compared with that of Farina's system ($Pd(dba)_2$/P(2-furyl)$_3$) in a set of experiments carried out under the same conditions. The relevant data collected in runs 7 and 8 of Table 7 show that while Farina's system affords slightly higher initial reaction rates, the systems with aryl substituted P-N ligands, such as **3** or **4**, provide higher final yields. Thus, it is evident that the iminophosphines are able to give more robust catalytic species.

A challenging aspect of the Stille reaction is to get reasonable coupling rates even with aryl bromides or aryl chlorides. When the catalytic system **3a/3** is used in THF at 50°C, the coupling of PhX with PhC≡CSnBu$_3$ proceeds only for X=I, no reaction being observed when X=Br or Cl. The use of dioxane as solvent allows to increase the reaction temperature at 90°C. Under these conditions, the coupling of PhBr with the alkynylstannane proceeds at a moderately good rate, while chlorobenzene is almost unreactive. The relevant data is collected in Table 8, and shows that, as usual, the relative reactivity of PhX decreases in the series X=I>Br>Cl.

The reaction of phenyl iodide with tributylphenylethynylstannane is a model reaction useful to investigate the effects due to the catalyst composition and the reaction conditions. However from the synthetic point of view the most useful application of the Stille reaction is the coupling of aryl halides with vinylstannanes. Therefore, we have also studied the coupling of iodobenzene with tributylvinylstannane (Eq. (3)) in order to better characterise the efficiency of the P-N/Pd catalytic systems.



(3)

Usually, the reactivity of stannanes in Stille coupling decreases in the order alkynyl≫vinyl>aryl>alkyl[5] and indeed, the coupling of tributylvinylstannane with iodobenzene proceeds very sluggishly at 50°C in THF. Suitable reaction rates were obtained working with a stannane/Pd ratio of 200:1 in dioxane at 90°C.

First, we checked the best P-N/Pd molar ratio for the reaction. Experiments carried out with the iminophosphines **3** and **4** revealed that using a molar ratio P-N/Pd 1:1 the initial reaction rates are much higher than those obtained at P-N/Pd 2:1 (Table 9); however, after an initial period in which the catalyst activity is very high, the reaction rate decreases. Accordingly, the product yields obtained after 24 h using 1 or 2 equiv. of iminophosphine are similar. The experiments also showed that the use of the preformed Pd(0) catalyst **3a** is equivalent to the use of $Pd(OAc)_2$ in combination with 1 or 2 equiv. of ligand **3**.

Table 9. Coupling of iodobenzene with tributylvinylstannane

Run	Catalyst	Added ligand	Ligand/Pd[a]	Yield (%) at different times			
				1 h	2 h	4 h	24 h
1	**3a**	–	1:1	42	57	71	89
2	**3a**	**3**	2:1	3	7	21	80
3	$Pd(OAc)_2$	**3**	1:1	45	55	64	79
4	$Pd(OAc)_2$	**4**	1:1	47	59	64	80
5	$Pd(OAc)_2$	**4**	2:1	5	8	30	83
6	$Pd(OAc)_2$	**1**	1:1	16	33	47	70
7	$Pd(OAc)_2$	**5**	1:1	34	41	55	76
8	$Pd(OAc)_2$	**6**	1:1	36	46	54	73
9	$Pd(OAc)_2$	**7**	1:1	20	29	39	67
10	$Pd(OAc)_2$	P(fur)$_3$	1:1	39	50	56	62
11	$Pd(OAc)_2$	P(fur)$_3$	2:1	66	69	76	86
12	$Pd(OAc)_2$	P(fur)$_3$	4:1	84	86	91	94

T: 90°C; solvent: dioxane (5 mL); PhI=CH_2≡CHSnBu$_3$=1.30 mmol; stannane/Pd=200:1.

[a] Total ligand/Pd molar ratio.

As far as the effect of the imino-nitrogen substituent R on the catalyst activity is concerned, it appears that the same factors observed with tributylphenylethynylstannane are also operative with tributylvinylstannane. As a matter of fact, the higher reaction rates are observed when R is phenyl (run 3) or *p*-methoxyphenyl groups (run 4), while the lowest product yields are obtained when R is an alkyl group (runs 6 and 9). However, it should be noted that the difference in reactivity observed with the various substituents R appears to be less wide than in the case of tributylphenylethynylstannane.

When compared with Farina's system (runs 10–12), the iminophosphines appear to be less active being unable to furnish the same initial reaction rates; however, while the activity of the P(2-furyl)$_3$ decreases rapidly with the time, the iminophosphine based systems appear more robust and provide higher final yields.

3. Conclusions

The data presented here demonstrates that iminophosphine–palladium complexes are very active catalytic systems for the Stille reaction. In particular, these systems provide reaction rates comparable or superior to those attainable with the trifurylphosphine–palladium(0) system, one of the most efficient catalysts known.

Two features of the catalysis appear particularly significant: (i) the reaction rate is markedly dependent on the imino-nitrogen substituent R, and (ii) the best ligand to palladium ratio is 2:1 with alkynylstannanes, while it is 1:1 with vinylstannanes.

These systems are particularly robust allowing very high product yields even at stannane/palladium ratios as high as 1000:1 with acetylenic substrates and 200:1 with vinyl ones.

The catalysts formed by adding 1 or 2 equiv. of iminophosphine to $Pd(OAc)_2$ appear particularly convenient for their prompt availability and stability.

As far as the mechanism of the reaction is concerned, Shirikawa has proposed a catalytic cycle involving the initial oxidative addition of the organostannane to a palladium(0)–iminophosphine species generated in situ.[13] We are currently investigating the mechanistic details in order to rationalise the effects on the reaction rate brought about by the presence of an activated olefin such as dimethylfumarate, the nature of the imino-nitrogen substituent and the change in the P-N/Pd molar ratio, and also to explain the lasting catalytic activity of these systems.

4. Experimental

4.1. Materials and instrumentation

^1H and ^{31}P NMR spectra were recorded on a Bruker AM 400 NMR spectrometer operating at 400.13 and 161.98 MHz, respectively. 85% phosphoric acid was used as external standard for ^{31}P NMR. GLC analyses were performed on a HP 5890 series II gas chromatograph, GC–MS analyses were obtained on a HP 5890 series II gas chromatograph interfaced to a HP 5971 mass-detector using the same type of column.

All the reactions, unless otherwise stated, were carried out under an inert atmosphere (argon).

The product yields reported in Tables were determined by GLC.

Aryl halides (Aldrich) and other commercial solvents (Aldrich or Fluka) were purified before the use following literature procedures.[22] $Pd(OAc)_2$ (Engelhard Industries), dibenzylideneacetone (Fluka), dimethylfumarate (Fluka), 4-trifluoromethylaniline (Aldrich), 4-fluoroaniline (Aldrich) and tributylvinylstannane (Fluka) were commercial products and used as received.

Tributylphenylethynylstannane,[23] tri(2-furyl)phosphines,[24] and $Pd(dba)_2$[25] were prepared as described in the literature. The iminophosphines 2-(PPh_2)-C_6H_4-1-CH=NR (R=Ph (**3**), CH_2CH_2Ph (**7**)) were prepared by published methods.[20] The iminophosphines 2-(PPh_2)-C_6H_4-1-CH=NR (R=CH_3 (**1**), CMe_3 (**2**), C_6H_4OMe-4 (**4**)) as well as the corresponding complexes [Pd(η^2-dmf){2-(PPh_2)-(C_6H_4-1-CH=NR}] (**1a**, **2a**, **4a**) were synthesised as described in Ref. 17.

4.1.1. Pd(η^2-dmf){2-(PPh_2)-C_6H_4-1-CH=NPh}] (3a). The synthetic procedure of Ref. 17 was used: the new complex was obtained as a yellow-orange solid in 73% yield. ^1H NMR ($CDCl_3$, δ): 3.14 (s, 3H), 3.25 (s, 3H), 3.51 (dd, J=10.0 Hz, 1H), 4.24 (dd, J=10.0 Hz, 1H), 7.1–7.6 (m, 19H), 8.12 (d, J=3.4 Hz, 1H); ^{31}P NMR ($CDCl_3$) δ: 22.1; ν_{max} (CH_2Cl_2) 1673 (C=O), 1610 (C=N) cm^{-1}; Anal. data: calcd for $C_{31}H_{28}NO_4PPd$: C, 60.45; H, 4.58; N, 2.27. Found: C, 60.5; H, 4.5; N, 2.3.

4.1.2. 2-(PPh_2)-C_6H_4-1-CH=NC_6H_4F-4 (5). 2-(Diphenylphosphino)benzaldehyde (1.00 g, 3.44 mmol) and the 4-fluoroaniline (1.25 g, 11.3 mmol) were dissolved in 80 mL of a MeOH/CH_2Cl_2 mixture (3/1 v/v) under nitrogen. The solution was stirred at room temperature, and the reaction progress was monitored by TLC. When the condensation was complete (ca. 20 h), the solvents were removed under reduced pressure and the residue purified by chromatography (silica gel, 20% ethyl ether in *n*-hexane (v/v)), followed by recrystallization in cold methanol (−20°C). Pale yellow solid (yield: 0.93 g, 70%). ^1H NMR ($CDCl_3$, ppm), δ: 6.85–7.00 (m, 11H), 7.25–7.40 (m, 5H), 7.43–7.50 (m, 1H), 8.15–8.20 (m, 1H), 9.03 (d, J=5.1 Hz, 1H); ^{31}P NMR ($CDCl_3$, ppm), δ: −10.2; ν_{max} (Nujol) 1623 (C=N), 1232 (C–F) cm^{-1}; Anal. data: calcd for $C_{25}H_{19}FNP$: C, 78.32; H, 4.99; N, 3.65. Found: C, 78.5; H, 5.0; N, 3.6.

4.1.3. 2-(PPh_2)-C_6H_4-1-CH=$NC_6H_4CF_3$-4 (6). This compound was prepared following the same procedure used for **5**. Pale yellow solid (yield: 1.23 g, 83%). ^1H NMR ($CDCl_3$, ppm), δ: 6.85–6.90 (m, 2H), 6.90–6.98 (m, 1H), 7.25–7.40 (m, 11H), 7.43–7.50 (m, 1H), 7.50–7.55 (m, 2H), 8.15–8.20 (m, 1H), 9.00 (d, J=5.1 Hz, 1H); ^{31}P NMR ($CDCl_3$, ppm), δ: −9.9; ν_{max} (Nujol) 1621 (C=N), 1320 (C–F) cm^{-1}; Anal. data: calcd for $C_{26}H_{19}F_3NP$: C, 72.05; H, 4.42; N, 3.23. Found: C, 72.3; H, 4.4; N, 3.3.

4.2. Catalytic experiments

The reactions were carried out in a jacketed glass reactor (volume ca. 30 mL) equipped with a reflux condenser, a side arm with stopcock for freeze-thaw cycles and with a threaded side port with rubber septum and cap for syringe sampling. The details for run 1 of Table 1 are reported as an example.

The reactor was charged under argon with 5 mL of THF, 510 mg (1.3 mmol) of tributylphenylethynylstannane, 150 μL (270 mg, 1.3 mmol) of iodobenzene, and 7.2 mg (0.013 mmol) of [Pd(dimethylfumarate)(Ph_2P-(C_6H_4CH=NCH_3)]. Then the reactor was heated at 50°C by circulating a thermostatic fluid through the outer jacket. After 2 h, the reaction mixture was cooled to rt and the crude reaction mixture analysed by GLC to determine substrate conversion and product yield.

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