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Synthesis, characterization and catalytic activity of new aminomethyldiphosphine–Pd(II) complexes for Suzuki cross-coupling reaction

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A new range of CF_3-substituted aminomethyldiphosphine (P—C—N) ligands ($(C_6H_5)_2PCH_2)_2NR$ (R = —C_6H_4(2-CF_3) (1a), —C_6H_4(3-CF_3) (1b) has been synthesized from 2-(trifluoromethyl)aniline and 3-(trifluoromethyl)aniline with diphenylphosphine. The aminomethyldiphosphine ligands were reacted with Pd(cod)Cl_2 to give corresponding metal complexes, $PdLCl_2$ (2a, 2b). The aminomethyldiphosphine–palladium compounds were characterized by utilizing several methods including NMR (^{1}H, ^{13}C, ^{31}P) and elemental analysis. These compounds were used as catalysts in Suzuki cross-coupling reaction of aryl chlorides and bromides. The effect of base was also investigated in this current project. CF_3-substituted aminomethyldiphosphine–palladium complexes were found to be efficient catalysts in Suzuki cross-coupling reaction of activated and deactivated aryl boronic acids. Copyright © 2013 John Wiley & Sons, Ltd.

Keywords: phosphine; palladium; Suzuki cross-coupling reaction; aryl halide

Introduction

The palladium-catalyzed Suzuki cross-coupling reactions have been increasingly employed for the formation of C—C bonds between aryl boronic acids and aryl halides.[1–4] In particular, this reaction is widely used as key intermediates in fine chemistry, for example pharmaceuticals, herbicides and natural products. Over the past 40 years, the chemistry of the Suzuki cross-coupling reaction has been the subject of intense study, and considerable effort has been devoted the synthesis of ligands and catalysts. It has been shown in the literature that choosing a solvent, catalysts and temperature conditions are quite important factors in increasing the yield of the product in the Suzuki reaction.[5–8] Previous studies showed that C—C bond formation is not achieved without using bases in the Suzuki cross-coupling reaction.[9] Also the genus of bases affects the conversion and increases the rate of C—C coupling reaction. In the Suzuki reaction it was reported that NaOAc, K_2CO_3, Cs_2CO_3, Na_2CO_3 and K_3PO_4 are used to determine optimum conditions for the Suzuki reaction.[10]

In general, the Suzuki reaction is carried out in the presence of palladium–phosphine catalysts since they are highly active and selective catalysts.[11–17] A range of catalysts have been synthesized to improve catalytic activity, selectivity and stability for the Suzuki reaction. Although phosphine ligands and their palladium complexes are widely used to catalyze the Suzuki cross-coupling reaction for a variety of substrates,[18–20] there are not many studies concerning the CF_3-substituted aminomethyldiphosphines[21] and their applications in Suzuki-type reactions.

In this study we have prepared new —CF_3-modified aminomethyldiphosphine (P—C—N) ligands (**1a**, **1b**) and their palladium(II) complexes (**2a**, **2b**) to be used in the Suzuki cross-coupling of aryl halides with aryl boronic acids. The results demonstrated that apart from aminomethyldiphosphine palladium complexes are easily synthesized and these compounds are efficient catalysts for the Suzuki cross-coupling reaction.

Experimental

Materials and Methods

All reactions were conducted under an inert atmosphere of N_2 or Ar using conventional Schlenk glassware. Diethyl ether, toluene and dichloromethane were dried using established procedures and then immediately distilled under nitrogen atmosphere prior to use. 2-(Trifluoromethyl)aniline and 3-(trifluoromethyl)aniline, obtained from Sigma-Aldrich Chemie GmbH (Steinheim, Germany), were used without further purification. [Pd(cod)Cl_2] was prepared as described in the literature.[22]

Elemental analysis was performed using a LECO CHNS 932 instrument. The ^{1}H NMR (400.1 MHz) and ^{31}P{^{1}H} NMR (162 MHz) spectra were recorded at 25 °C in DMSO-d^6 and $CDCl_3$ on a Bruker NMR spectrometer; ^{13}C NMR were recorded on a Varian Mercury 100.6 MHz NMR spectrometer. ^{31}P{^{1}H} NMR spectra were recorded with complete proton decoupling and reported in ppm using 85% H_3PO_4 as external standard. The coupling products were analyzed by a PerkinElmer Clarus 500 series gas chromatograph equipped with a flame ionization detector and a 30 m × 0.25 mm × 0.25 μm film thickness β-Dex capillary column. Thin-layer chromatography was used for monitoring the reactions.

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Preparation of Ligands and Complexes

*Preparation of ($(Ph_2PCH_2)_2NC_6H_4$—2-(CF_3)) (**1a**)*

A mixture of Ph_2PH (1.5 mL, 8.0 mmol), HCHO (0.8 mL, 14 mmol), and 2-(trifluoromethyl)aniline (0.65 g, 4 mmol) was refluxed for 2 h in toluene (10 mL). The reaction mixture was then allowed to cool to room temperature. The product was extracted with CH_2Cl_2, dried over $MgSO_4$ and filtered off. The filtrate was evaporated under reduced pressure until dryness to give the title compound **1a**, 1.65 g (74%). ^{1}H NMR (400.1 MHz, $CDCl_3$), δ ppm: 7.82–7.75 (m, 21H, CH, arom.), 7.46–7.41 (m, 1H, CH, arom.), 7.38–7.33(m, 1H, CH, arom.), 7.15–6.92 (m, 1H, CH, arom.), 4.04 (d, J = 4.3 Hz, 4H, CH_2). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ ppm: 149.19 (C_1, ArC—N), 136.40 (d, J_{PC} = 14.4 Hz), 133.15 (d, J_{PC} = 18.8 Hz), 132.18 (C_3), 131.86 (CH), 131.36 (d, J_{PC} = 9.3 Hz), 130.79 (C_4,CH), 129.32 (CH), 128.79 (d, J_{PC} = 6.6 Hz), 125.03 (C_6, C_2), 122.32 (CF_3) 55.67 (d, J_{PC} = 13.1 Hz, N—CH_2—P). ^{31}P NMR (162 MHz, $CDCl_3$), δ ppm: −18.84 ($\underline{P}Ph_2$). Anal. calcd for $C_{33}H_{28}F_3NP_2$: C, 71.09; H, 5.06; N, 2.51 %. Found: C, 70.43; H, 5.62; N, 2.62%.

The ligand **1b** was prepared as described in procedure **1a**.

*Preparation of ($(Ph_2PCH_2)_2NC_6H_4$—3-(CF_3)) (**1b**)*

Yield 1.60 g (71%).^{1}H NMR (400.1 MHz, $CDCl_3$), δ ppm: 7.55–7.44 (m, 20H, CH, arom.), 6.85–7.28 (m, 4H, CH, arom.), 3.84 (d, J = 4.9 Hz., 4H, CH_2). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ ppm: 144.20 (C_1, ArC—N), 132.63 (d, J_{PC} = 13.8 Hz), 131.56 (d, J_{PC} = 12.1 Hz), 131.35 (C_3), 131.12 (CH), 130.71 (d, J_{PC} = 11.4 Hz), 129.00 (C_4, CH), 128.87 (CH) 127.92 (d, J_{PC} = 7.1 Hz), 128.46 (C_6, C_2), 128.28 (CF_3), 60.70 (d, J_{PC} = 12.0 Hz, N—CH_2—P). ^{31}P NMR (162 MHz, $CDCl_3$), δ ppm: −19.25 ($\underline{P}Ph_2$). Anal. calcd for $C_{33}H_{28}F_3NP_2$: C, 71.09; H, 5.06; N, 2.51%. Found: C, 70.14; H, 4.92; N, 2.84%.

*Preparation of [$PdCl_2$ ($(Ph_2PCH_2)_2NC_6H_4$—2-(CF_3))] (**2a**)*

To a solution of [Pd(cod)Cl_2] (0.10 g, 0.35 mmol) in CH_2Cl_2 (10 mL) was added **1a** (0.20 g, 0.36 mmol). The mixture was stirred for 6 h at reflux. Then, addition of diethyl ether caused the formation of a yellow solid, which was filtered off and dried to give the title compound **2a**. Yield 0.17 g (80%), m.p. 158–159 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$), δ ppm: 7.95–7.71 (m, 20H, CH, arom.), 7.57–7.45 (m, 1H, CH, arom.), 7.40–7.35 (m, 1H, CH, arom.), 7.32–7.26 (m, 1H, CH, arom.), 4.40 (d, J = 1.8 Hz, 4H, CH_2). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ ppm: 146.43 (C_1, ArC—N), 139.36 (C_9), 132.23 (C_5), 132.09 (C_{10}, C_{14}), 131.84 (C_{11}, C_{12}, C_{13}), 131.77 (C_3), 130.98 (C_4), 128.56 (C_6) 127.90 (CF_3), 55.82 (C_7, C_8, N—CH_2—P). ^{31}P NMR (162 MHz, $CDCl_3$), δ ppm: 8.03 (Pd—PPh_2). Anal. calcd for $C_{33}H_{28}Cl_2F_3NP_2Pd$: C, 53.94; H, 3.84; N, 1.91%. Found: C, 55.01; H, 3.92; N, 2.14%.

The complex **2b** was prepared as described for procedure **2a**.

*Preparation of [$PdCl_2$($(Ph_2PCH_2)_2NC_6H_4$—3-(CF_3))] (**2b**)*

Yield 0.15 g (78%), m.p. 248–250 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$), δ ppm: 7.52–7.09 (m, 20H, CH, arom.), 7.88–7.70 (m, 4H, CH, arom.), 4.43 (d, J = 2.1 Hz, 4H, CH_2). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ ppm: 148.82 (C_1, ArC—N), 137.59 (C_9), 132.37 (C_5), 132.02 (C_{10}, C_{14}), 131.69 (C_{11}, C_{12},C_{13}), 130.81 (C_2), 130.72 (C_4), 129.06 (C_6) 126.90 (CF_3), 59.21 (C_7, C_8, N—CH_2—P). ^{31}P NMR (162 MHz, $CDCl_3$), δ ppm: 9.56 (Pd—PPh_2). Anal. calcd for $C_{33}H_{28}Cl_2F_3NP_2Pd$: C, 53.94; H, 3.84; N, 1.91%. Found: C, 54.74; H, 4.08; N, 2.10%.

General Procedure for Suzuki Cross-Coupling

An oven-dried Schlenk flask was charged with base (2 mmol) and organic solvent–H_2O (3/3 mL) under nitrogen atmosphere followed by aryl halide (1 mmol), aryl boronic acid (1.5 mmol) and Pd(II) catalyst (1 mol%). The flask was then sealed under N_2 atmosphere and placed in an oil bath pre-heated at 80 °C. The reaction mixture was stirred and then allowed to cool to room temperature. The reaction mixture was poured into water (5 mL) and extracted with $CHCl_3$ (3 × 20 mL). The extracts were washed with brine and dried over $MgSO_4$ and solvent was evaporated.

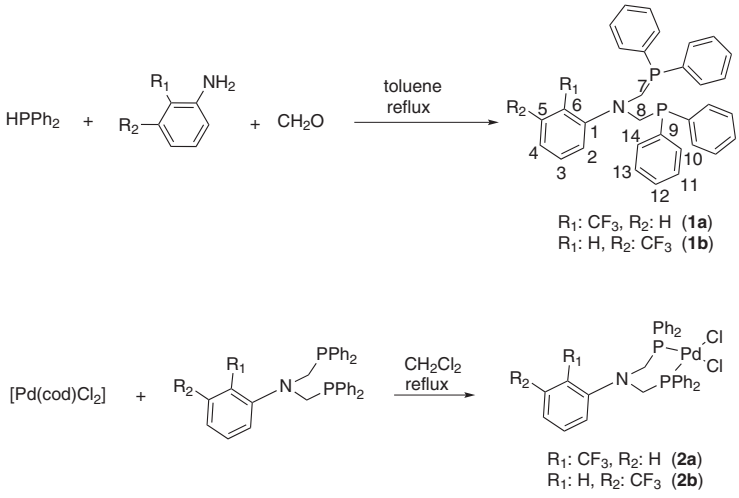
Results and Discussion

Ligands **1a** and **1b** were synthesized by treating diphenylphosphine ($HPPh_2$) with appropriate CF_3-substituted anilines according to the Mannich reaction. The Pd(II) complexes of the aminomethyldiphosphine ligands (**2a**, **2b**) were prepared under argon atmosphere using Schlenk techniques as shown in Scheme 1.

Characterization of CF_3-Substituted Aminomethyldiphosphine Ligands and their Pd(II) Complexes

The structures of compounds (**1a–2b**) were characterized by the ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and elemental analysis.

It was found that although the metal complexes (**2a**, **2b**) are very soluble in CH_2Cl_2, $CHCl_3$, CH_3CH_2OH and acetone, they are insoluble in diethyl ether and *n*-hexane. These complexes are stable both in air and in organic solvent. The ^{1}H NMR spectra of the ligands (**1a**, **1b**) and their Pd(II) complexes (**2a**, **2b**) showed that the protons of the phenyl ring were at 6.92–7.95 ppm. The ^{1}H NMR spectrum of ligands and their Pd(II) complexes **1a–2b** appear at 3.84–4.43 ppm, corresponding to the methylenic (P$\underline{C}H_2$N) protons respectively. Additionally, there is no remarkable difference between the free ligands and their Pd(II) complexes in the ^{1}H NMR spectra. The NCH_2P signals of **2a** and **2b** slightly shifted downfield when compared to the free ligands **1a** and **1b**. As a result of this, the N atom was not coordinated to Pd(II) as reported in the literature.[23,24] The ^{31}P{^{1}H} NMR spectra of all compounds (**1a–2b**) manifested that a singlet



Scheme 1. Synthesis of CF_3-substituted aminomethyldiphosphine ligands and their Pd(II) complexes.

Table 1. ^{31}P NMR data for ligands and Pd(II) complexes

Compound	δ_p (ppm)	$\Delta\delta$ (ppm)[a]
1a	−18.8	—
1b	−19.2	—
2a	8.0	26.9
2b	9.5	28.8

[a] ^{31}P chemical shifts $\Delta\delta$ (ppm) = δ(complex) − δ (ligand).

resonance shifted downfield when compared to the uncoordinated aminomethyldiphosphines, as shown in Table 1. The coordination shift values of the complexes (Δ) depending on the metal centers and the chemical structures of the ligands showed that the ligands coordinated to Pd(II) via phosphorus atoms to give chelated complexes.[25]

Elemental analysis for C, H and N of ligands **1a**, **1b** and Pd(II) metal complexes **2a**, **2b** indicated that the metal–ligand ratio of complexes was 1:1.

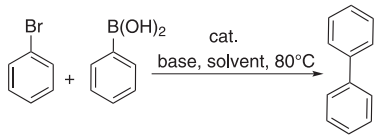
Suzuki Reaction

The catalytic activity of Pd(II) complexes was tested for the Suzuki coupling reactions. The results obtained for the Suzuki reaction of aryl bromides and chlorides in the presence of phenylboronic acid are summarized in Tables 2 and 3. Our group has previously studied the reaction of phenylboronic acid with bromobenzene in different organic solvents and bases, e.g. DMF, toluene, 1,4-dioxane, K_2CO_3, NaOAc and Cs_2CO_3. It was found that K_2CO_3 and NaOAc were useful bases in these reactions at 80 °C. Cs_2CO_3 is also an effective base in the reactions as shown in Table 2, but it is an expensive compared to the other bases. The results in Tables 2 and 3 illustrate that **2a** shows slightly higher activity than **2b**.

According to the data presented in Table 3, under the same reaction conditions catalysts **2a** and **2b** both exhibited excellent activity and 99% biphenyl was obtained in the event of chlorobenzene. These results show that both CF_3-substituted aminomethyldiphosphine–Pd(II) complexes (**2a**, **2b**) are active catalysts for the Suzuki cross-coupling reaction.

Finally, we checked the activity of complexes **2a** and **2b** in the cross-coupling reaction of different phenylboronic acids and aryl halide (Tables 4 and 5). As can be seen from Table 4, 2**a** and 2**b** catalysts exhibited the highest catalytic activity. As is obvious from Table 4, the Suzuki cross-coupling reaction displayed the Pd(II) complexes of chelating bidentate ligands as efficient catalysts. Owing to the electron-withdrawing nature of the trifluoromethyl group and its being far away from the phosphorus atom, the electron density of the phosphorus center is not affected very much. Therefore, the Suzuki reaction that was carried out with aryl chloride gave good results. During the catalytic

Table 2. Palladium-catalyzed coupling of bromobenzene with phenylboronic acid[a]

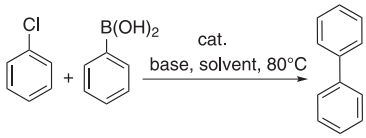


Entry	Catalyst	Base	Solvent	Time (h)	Yield[b] (%)
1	**2a**	K_2CO_3	1,4-Dioxane	1	99
2	**2a**	K_2CO_3	DMF	2	93
3	**2a**	K_2CO_3	Toluene	2	99
4	**2a**	NaOAc	1,4-Dioxane	1	99
5	**2a**	NaOAc	DMF	1	78
6	**2a**	NaOAc	Toluene	3	46
7	**2a**	Cs_2CO_3	1,4-Dioxane	3	35
8	**2a**	Cs_2CO_3	DMF	2	98
9	**2a**	Cs_2CO_3	Toluene	1	69
10	**2b**	K_2CO_3	1,4-Dioxane	1	98
11	**2b**	K_2CO_3	DMF	2	95
12	**2b**	K_2CO_3	Toluene	6	99
13	**2b**	NaOAc	1,4-Dioxane	1	98
14	**2b**	NaOAc	DMF	1	97
15	**2b**	NaOAc	Toluene	2	86
16	**2b**	Cs_2CO_3	1,4-Dioxane	1	77
17	**2b**	Cs_2CO_3	DMF	2	95
18	**2b**	Cs_2CO_3	Toluene	5	99

[a] Reaction conditions: aryl halide (1 mmol), phenylboronic acid (1.2 mmol) base (1.2 mmol) and 0.01 mmol catalyst in 3/3 ml organic solvent/H_2O, 80 °C.

[b] All reactions were monitored by gas chromatography and yields are based on aryl halide.

Table 3. Palladium-catalyzed coupling of chlorobenzene with phenylboronic acid[a]

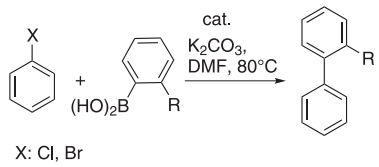


Entry	Catalyst	Base	Solvent	Time (h)	Yield[b] (%)
1	**2a**	K_2CO_3	1,4-Dioxane	17	99
2	**2a**	K_2CO_3	DMF	24	91
3	**2a**	K_2CO_3	Toluene	14	54
4	**2a**	NaOAc	1,4-dioxane	17	82
5	**2a**	NaOAc	DMF	24	58
6	**2a**	NaOAc	Toluene	19	94
7	**2a**	Cs_2CO_3	1,4-Dioxane	17	99
8	**2a**	Cs_2CO_3	DMF	18	29
9	**2a**	Cs_2CO_3	Toluene	24	91
10	**2b**	K_2CO_3	1,4-Dioxane	24	99
11	**2b**	K_2CO_3	DMF	18	15
12	**2b**	K_2CO_3	Toluene	17	93
13	**2b**	NaOAc	1,4-Dioxane	7	65
14	**2b**	NaOAc	DMF	18	61
15	**2b**	NaOAc	Toluene	31	84
16	**2b**	Cs_2CO_3	1,4-Dioxane	24	95
17	**2b**	Cs_2CO_3	DMF	18	26
18	**2b**	Cs_2CO_3	Toluene	14	97

[a] Reaction conditions: aryl halide (1 mmol), phenylboronic acid (1.2 mmol), base (1.2 mmol) and 0.01 mmol catalyst in 3/3 ml organic solvent/H_2O, 80 °C.

[b] All reactions were monitored by gas chromatography and yields are based on aryl halide.

Table 4. Palladium-catalyzed coupling of aryl halide with 2-substituted phenylboronic acids[a]

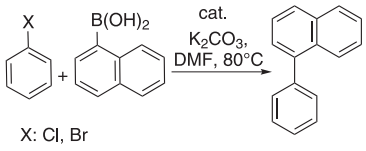


Entry	Catalyst	X	R	Time (h)	Yield[b] (%)
1	**2a**	Cl	—CH_3	7	98
2	**2a**	Cl	C_6H_5	7	99
3	**2a**	Br	—CH_3	2	99
4	**2a**	Br	C_6H_5	3	35
5	**2b**	Cl	—CH_3	8	96
6	**2b**	Cl	C_6H_5	16	52
7	**2b**	Br	—CH_3	3	98
8	**2b**	Br	C_6H_5	3	78

[a]Reaction conditions: aryl halide (1 mmol), phenylboronic acid (1.2 mmol) base (1.2 mmol) and 0.01 mmol catalyst in 3/3 ml DMF/H_2O, 80 °C.

[b]All reactions were monitored by gas chromatography and yields are based on aryl halide.

Table 5. Palladium catalyzed coupling of arylhalide with naphtaleneboronic acid[a]



Entry	Catalyst	X	Time (h)	Yield[b] (%)
1	**2a**	Cl	11	40
2	**2a**	Br	2	50
3	**2b**	Cl	11	35
4	**2b**	Br	2	99

[a]Reaction conditions: aryl halide (1 mmol), phenylboronic acid (1.2 mmol) base (1.2 mmol) and 0.01 mmol catalyst in 3/3 ml DMF/H_2O, 80 °C.

[b]All reactions were monitored by gas chromatography and yields are based on aryl halide.

cycle, activation of the Pd(II) precursor by phenyl boronic acid is also very rapid, even with very electron-rich ligands.

Conclusions

Pd(II) complexes with new CF_3-substituted aminomethyldiphosphine (P—C—N) ligands have been synthesized and characterized using spectroscopic techniques. $^{31}P\{^1H\}$ NMR spectra of the complexes indicate that coordination of the aminomethylphosphine ligand occurs via two phosphorus atoms. The complexes have been tested as catalysts for the Suzuki reaction. The results show that complexes **2a** and **2b** catalyzed the reaction of olefin with aryl halide in excellent yields.

In the next step, we have scheduled to synthesize —C_8F_{17}-included aminomethyldiphosphine ligands instead of —CF_3 and their Pd(II) complexes. Additionally these complexes may be examined in the C—C coupling reactions in supercritical CO_2 solvent systems as a catalyst.

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