Synthesis of novel (bis)(diarylamino)thiophenes *via* palladium-catalysed reaction of (di)bromothiophenes with diarylamines

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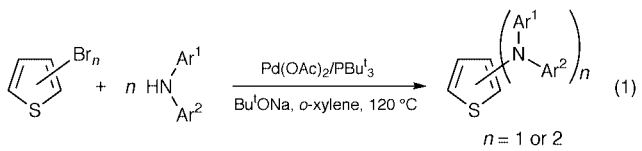
Synthesis of novel (bis)(diarylamino)thiophenes including 2,5-bis(diarylamino)thiophenes was attained by PBu^t_3-ligated palladium-catalysed coupling of (di)bromothiophenes with diarylamines.

Thiophene-containing compounds are widely known as an important class of materials which show intrinsic electronic properties such as luminescence,[1,2] redox activity,[3] nonlinear optical chromism[4] and electron-transport.[5] While triarylamines generally bear a role of hole-transport for organic electroluminescent (EL) display devices,[6] thienylphenylene-containing triarylamines showed different properties.[1,4] Thus, incorporation of a thiophene moiety into the triarylamine system is of current interest due to the product's potential applications. Nevertheless, synthesis of triarylamines bearing thienylamino group(s) is quite rare. 1,3,5-Tris(*N*-phenylthienylamino)benzenes have been synthesized by Ullmann coupling of tris(phenylamino)benzene and 2- and 3-iodothiophenes,[7] but there have been no reports of the synthesis of other (diarylamino)thiophenes.

Palladium-catalysed amination technology is widely known as a useful synthetic method for making arylamines from aryl halides with amines, and has been intensively examined for the synthesis of a wide range of arylamines since Buchwald and Hartwig reported the reaction.[8] However, halothiophenes have not been employed as substrates for the amination reaction. On the other hand, we recently reported that PBu^t_3 served as an excellent ligand for palladium-catalysed amination of aryl halides.[9] The catalytic system consisting of a palladium compound and PBu^t_3 also showed exceedingly high catalytic activity in the synthesis of triarylamines.[10] Herein we report the first palladium-catalysed synthesis of novel (diarylamino)thiophenes and 2,5-bis(diarylamino)thiophenes from (di)bromothiophenes and diarylamines [eqn. (1)].



(1)

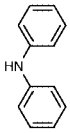
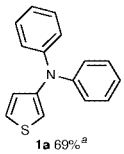
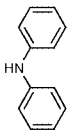
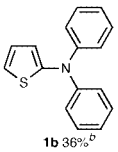
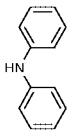
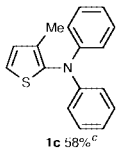
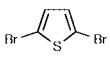
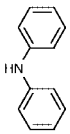
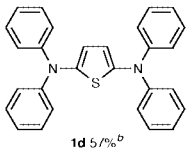
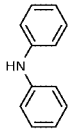
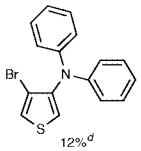
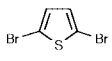
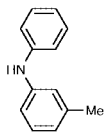
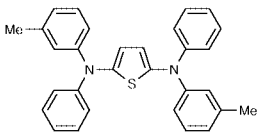
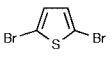
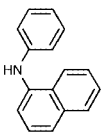
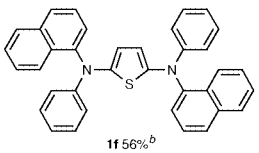
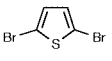
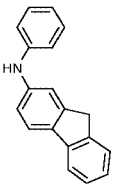
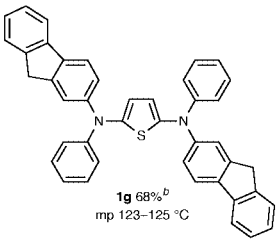
The coupling of (di)bromothiophenes with diarylamines is most suitable for synthesizing (bis)(diarylamino)thiophenes because (di)bromothiophenes are commercially available and inexpensive. The coupling reaction was examined using Bu^tONa in *o*-xylene at 120 °C (Table 1).† Reaction of 3-bromothiophene with Ph_2NH smoothly proceeded in the presence of 0.25 mol% of $Pd(OAc)_2$ to afford 69% yield of 3-(diphenylamino)thiophene **1a** (entry 1). On the other hand, although 0.75 mol% palladium catalyst was required to give complete conversion of 2-bromothiophene (entry 2), the reaction with Ph_2NH gave the desired product using a small amount of the catalyst. 2-Bromo-3-methylthiophene was similarly coupled without any significant steric effect due to the methyl group (entry 3). Double amination of dibromothiophene with diarylamines gives larger molecules of bis(diarylamino)thiophenes with higher molecular weight, which can be expected to be morphologically more stable than mono(diarylamino)thiophenes for organic EL devices. The palladium catalyst was so active that 2,5-dibromothiophene in the reaction with Ph_2NH could be converted to 2,5-bis(diphenylamino)thiophene **1d** in 57% yield in the presence of 2 mol% of palladium catalyst per dibromothiophene (entry 4). When 2 mol% of $Pd(dba)_2$/BINAP was used as catalyst in the same reaction, the catalytic activity was low, and after 24 h at 120 °C, 2-bromo-5-(diphenylamino)thiophene and 2,5-bis(diphenylamino)thiophene were obtained in 34 and 6% GC yield, respectively. These results indicate that PBu^t_3, which is a bulky and electron-rich phosphine, facilitates the amination of highly electron-rich aryl halides. Reaction of 3,4-dibromothiophene with Ph_2NH was also attempted and gave only a 12% yield of 3-bromo-4-(diphenylamino)thiophene, which is the monoamination product (entry 5). Using the same catalyst, reaction of *o*-dibromobenzene with Ph_2NH gave no product.[10] Although amination of 3,4-dibromothiophene afforded a low yield of monoaminated product, the difference in the reactivity between 3,4-dibromothiophene and *o*-dibromobenzene may be ascribed to the difference of the angle of C–C–Pd bond of the resulting arylpalladium complex after oxidative addition, in which the intramolecular coordination of a vicinal bromine to the palladium complex obtained from *o*-dibromobenzene is more likely to prevent Ph_2NH from ligating to the Pd complex. The coupling of 2,5-dibromothiophene with other diarylamines such as 3-methyldiphenylamine and *N*-phenyl-1-naphthylamine was performed to give 2,5-bis(diarylamino)thiophenes (**1e** and **1f**) (entries 6 and 7). 2,5-Bis(*N*-phenyl-2-fluorenylamino)thiophene **1g** could be prepared by Pd-catalysed reaction of 2-bromofluorene with aniline followed by addition of 2,5-dibromothiophene to the resulting reaction mixture (entry 8). Therefore, this synthetic method can be applied to the synthesis of a variety of elaborate diarylaminothiophenes with aromatic fused ring systems *via* secondary arylamines.

We have demonstrated that the catalytic system consisting of a palladium compound and PBu^t_3 catalysed coupling of bromothiophenes and diarylamines to afford novel (bis)(diarylamino)thiophenes in good yields. Although 2(,5)-(di)bromothiophenes were presumed not to undergo the amination reaction due to their strong coordination to the palladium catalyst, this catalytic system allows the amination with diarylamines to occur in the presence of a small amount of catalyst. The employment of PBu^t_3, which is a bulky and electron-rich ligand, realised the Pd-catalysed formation of (bis)(diarylamino)thiophenes.

Notes and references

† *General procedure*: $Pd(OAc)_2$ (44.9 mg, 0.2 mmol), PBu^t_3 (2.4 ml, 50 mg ml^{-1} in *o*-xylene, 121.4 mg, 0.6 mmol), 2,5-dibromothiophene (2.42 g, 10 mmol), diarylamine (20 mmol), sodium *tert*-butoxide (2.11 g, 22 mmol) and *o*-xylene (40 ml) were mixed at room temperature and heated at 120 °C for 3 h under N_2. After addition of water and extractive work-up with Et_2O, *o*-xylene was stripped off *in vacuo*. The residue was purified by reprecipitation by adding MeOH (30 ml) for **1a** (1.73 g, 6.9 mmol), **1b** (0.90 g, 3.6 mmol), **1d** (2.39 g, 5.7 mmol), **1f** (2.90 g, 5.6 mmol) or column chromatography on Al_2O_3 (eluent; hexane–EtOAc = 100 : 0–1 : 1) for **1c**

Table 1 Palladium-catalysed synthesis of (bis)(diarylamino)thiophenes[a]

Entry	Substrate	Diarylamine	Product
1			 **1a** 69%[e] mp 91–92 °C
2			 **1b** 36%[b] mp 77–79 °C
3			 **1c** 58%[c] mp 66–67 °C
4			 **1d** 57%[b] mp 144–145 °C
5			 12%[d]
6			 **1e** 81%[c] oil
7			 **1f** 56%[b] mp 120–125 °C
8[e]			 **1g** 68%[b] mp 123–125 °C

[a] All reactions were performed in *o*-xylene with 0.25–2.0 mol% $Pd(OAc)_2$, 0.75–6 mol% PBu^t_3 and 1.1–2.2 equiv. of Bu^tONa at 120 °C for 3 h unless otherwise stated. Satisfactory spectral (^1H and ^{13}C NMR and mass) analyses data were obtained for each isolated compound. [b] Isolated yield by reprecipitation with MeOH, which is not optimised, [c] Isolated yield by column chromatography on Al_2O_3 (hexane–EtOAc = 100:0–1:1). [d] Determined by GC analysis. [e] The reaction was conducted at 120 °C for 24 h *in situ* after preparation of *N*-phenylfluoren-2-ylamine by Pd-catalysed reaction of aniline with 2-bromofluorene at 120 °C for 3 h.

(1.54 g, 5.8 mmol), **1e** (3.62 g, 8.1 mmol) and **1g** (4.04 g, 6.8 mmol). *Selected data* for **1a**: $\delta_H(CDCl_3)$ 6.62 (s, 1H), 6.86 (d, *J* 6.1, 1H). 6.98 (t, *J* 7.8, 2H), 7.08 (d, *J* 7.8, 4H), 7.14–7.24 (m, 5H); $\delta_C(CDCl_3)$ 113.00, 122.21, 123.52, 125.04, 129.02, 146.30, 148.01; *m/z* 251 (M^+). For **1b**: $\delta_H(CDCl_3)$ 6.71 (s, 1H), 6.85 (d, *J* 6.1, 1H), 6.92–7.04 (m, 3H), 7.13 (d, *J* 7.8, 4H), 7.24 (t, *J* 7.8, 4H); $\delta_C(CDCl_3)$ 121.05, 121.70, 122.40, 123.02, 126.02, 129.03, 148.32, 151.20; *m/z* 251 (M^+). For **1c**: $\delta_H(CDCl_3)$ 1.94 (s, 3H), 6.78 (d, *J* 6.1, 1H), 6.96 (d, *J* 7.7, 2H), 7.01–7.10 (m, 5H), 7.22 (t, *J* 7.7, 4H); $\delta_C(CDCl_3)$ 13.12, 121.22, 122.05, 122.10, 128.86, 129.02, 132.64, 143.62, 147.13; *m/z* 265 (M^+). For **1d**: $\delta_H(CDCl_3)$ 6.46 (s, 2H), 7.01 (t, *J* 7.7, 4H), 7.14 (d, *J* 7.7, 8H), 7.24 (t, *J* 7.7, 8H); $\delta_C(CDCl_3)$ 120.10, 122.65, 123.00, 129.52, 145.45, 147.80; *m/z* 418 (M^+). For **1e**: $\delta_H(CDCl_3)$ 2.26 (s, 6H), 6.64 (s, 2H), 6.82 (d, *J* 7.4, 2H), 6.90–6.99 (m, 6H), 7.10–7.16 (m, 6H), 7.23 (t, *J* 7.4, 4H); $\delta_C(CDCl_3)$ 21.56, 119.91, 122.27, 122.65, 123.34, 123.98, 129.11, 139.04, 145.60, 148.02; *m/z* 446 (M^+). For **1f**: $\delta_H(CDCl_3)$ 6.43 (s, 2H), 6.83 (t, *J* 7.8, 2H), 6.89 (d, *J* 7.8, 4H), 7.10 (t, *J* 7.8, 4H), 7.30–7.52 (m, 8H), 7.75 (d, *J* 7.7, 2H), 7.84 (d, *J* 7.7, 2H), 7.98 (d, *J* 7.7, 2H); $\delta_C(CDCl_3)$ 117.93, 118.78, 118.97, 120.59, 123.99, 126.28, 126.34, 126.57, 127.11, 128.45, 128.95, 130.81, 135.19, 143.08, 145.42, 149.33; *m/z* 518 (M^+). For **1g**: $\delta_H(CDCl_3)$ 3.79 (s, 4H), 6.49 (s, 2H), 6.98 (t, *J* 7.4, 2H), 7.10–7.38 (m, 16H), 7.45 (d, *J* 7.4, 2H), 7.63 (d, *J* 8.1, 2H), 7.66 (d, *J* 7.4, 2H); $\delta_C(CDCl_3)$ 36.95, 119.43, 119.83, 120.43, 122.06, 122.15, 122.62, 124.93, 126.10, 126.80, 129.18, 137.24, 141.41, 143.13, 144.58, 145.63, 146.84, 148.21; *m/z* 594 (M^+).

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