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Note

# Synthesis of 1′,1‴-bis(heterocyclyl)biferrocene compounds

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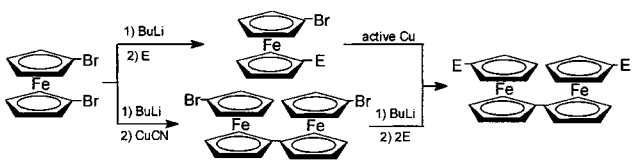
**Abstract**

A new method for preparing 1′,1‴-disubstituted heterocyclylbiferrocene derivatives via stepwise Stille coupling reaction of 1,1′-bis(tributylstannyl)ferrocene with heterocyclic bromides and subsequent Cu-catalyzed homocoupling reaction is established.


*Keywords:* Ferrocene; Stille coupling; Homocoupling; Heterocyclylbiferrocene

## 1. Introduction

The applications of heterocyclyl ferrocene derivatives in electrochemistry, materials science and biochemistry are well known [1–3]. In these areas of study biferrocene-type compounds are perhaps attractive candidates [4–18]. Dong and co-workers [10–18], in recent years, have reported a series of studies on the electron-transfer rate in mixed-valance biferrocenium salts and established two effective methods for the synthesis of 1′,1‴-disubstituted biferrocene derivatives [17,18]. One is selective lithium–bromine exchange of 1,1′-dibromoferrocene, followed by an electrophilic attack and finally homocoupling under active Cu [17]. Another is direct coupling of 1,1′-dibromoferrocene, using CuCN and oxygen as the coupling reagents, subsequently lithium–bromine exchange and finally by an electrophilic attack to give the desired products [18] as shown in Scheme 1. The disadvantages of these procedures are: (i) dibromoferrocene is tedious to prepare; (ii) lithium–bromine exchange needs drastic condition; and (iii) active lithioferrocene intermediate cannot tolerate many active groups such as amino, hydroxy and the like, which are bonded on electrophilic reagents. In addition, owing to the methodological limitation in their preparation, substituents on 1′ and 1‴ position were mostly simple groups.




Scheme 1.

In continuation of our studies [19–21] on the synthesis of ferrocenyl heterocyclic derivatives, our interest is in developing different methods for the synthesis of varied heterocyclyl ferrocene compounds using 1,1′-bis(tributylstannyl)ferrocene as the starting material. In present literature, no biferrocene compounds bearing heterocyclyl directly bonded on 1′ and 1‴ position are reported so far. This paper is concerned with the preparation of this type of compounds.

## 2. Results and discussion

1,1′-Bis(tributylstannyl)ferrocene (**1**) was obtained following the literature procedure [22,23]. This was found not only to undergo selective transmetalation

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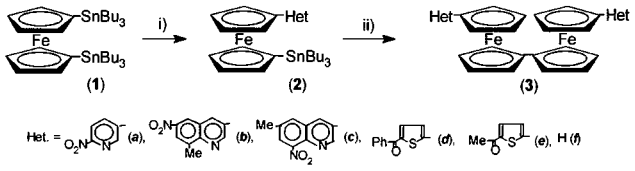


Scheme 2. (i) Het-Br 150% of **1** and 0.5% of $PdCl_2(PPh_3)_2$ in DMF at 100–200 °C heated for 1–1.5 h. (ii) **2** and stoichiometrical $CuSO_4 \cdot 3H_2O$ in THF stirred at r.t. for 1–8 h.

Table 1
Results of stepwise Stille coupling and subsequent homocoupling

| Entry | Time (h) | Products | Yield (%) | Melting point (°C) |
|---|---|---|---|---|
| *Stille coupling* | | | | |
| 1 | 1 | **2a** | 70 | |
| 2 | 1.5 | **2b** | 73 | |
| 3 | 1.5 | **2c** | 71 | |
| 4 | 1 | **2d** | 75 | |
| 5 | 1 | **2e** | 65 | |
| *Homocoupling* | | | | |
| 6 | 10 | **3a** | 90 | 158–159 |
| 7 | 8 | **3b** | 85 | 166 (dec.) |
| 8 | 8 | **3c** | 88 | 196 (dec.) |
| 9 | 10 | **3d** | 60 | 128–130 |
| 10 | 13 | **3e** | 45 | 82–84 |
| 11 | 40 min | **3f** | 96 | 283 (dec.) |

/c> >**3f**ca = "D" > >96ca = "D" > >283 (dec.)

reaction but also a smooth stepwise Stille across-coupling reaction, and has been judged to be one of the excellent starting material for the preparation of 1,1′-disubstituted ferrocene derivatives via these reactions [21–23]. Various 1-heterocyclyl-1′-tributylstannylferrocenes (**2**) could be easily obtained via the selective monosubsituted Stille coupling and the intermediates can subsequently be used as precursors for the preparation of title compounds (**3**) as indicated in Scheme 2.

Treatment of an excess of **1** with appropriate heterocyclic bromides under $PdCl_2(PPh_3)_2$ in dry DMF at 100–120 °C gave **2** in satisfactory yields (entries 1–5) as a deep red oil along with some monosubstituted heterocyclylferrocene as by-products.

Homocoupling of organostannanes have been recognized as one of the useful synthetic methods to form symmetrical biaryl, 1,3-dienes and 1,3-diynes [24–26]. Copper-promoted homocoupling was initially investigated by the coupling of tributylstannylferrocene itself (entry 11). The use of $Cu^{2+}$ promoted the desired homocoupling by stirring the mixture of tributylstannylferrocene and stoichiometrical amount of $CuSO_4 \cdot 3H_2O$ in THF at room temperature. The desired product, biferrocene, was obtained quickly in almost quantity yield. Other compounds (**3**) were obtained by the same procedure in satisfactory yields (entries 6–10), along with a little destannylation product, monosubstituted heterocyclylferrocene, as by-product. The results are summarized in Table 1.

Compared with Dong's procedure, our method has several advantages: (i) basic substrate, 1,1′-bis(tributylstannyl)ferrocene, is easily obtained under ordinary laboratory conditions in high yield (80%) or can be directly purchased; (ii) reaction condition is mild and simple; and (iii) it can tolerate all kinds of active groups.

1,1′-Bis(tributylstannyl)ferrocene was shown to be a good starting material for the synthesis of various functionalized 1′,1‴-bis(heterocyclyl)ferrocene compounds via two-step coupling, which are otherwise difficult to obtain.

## 3. Experimental

### 3.1. General

Melting points were determined on a Thomas Hoover capillary melting point apparatus and were uncorrected. $^1$H-NMR spectra were measured on a FC-80A spectrometer in $CDCl_3$ with $Me_4Si$ as the internal standard. Mass spectra (MS) were taken on Finnigan TQ70 or HP-5988 AG CMS mass spectrometer. IR spectra were recorded on a Nicolet 179SX FT-IR spectrometer as KBr pellets.

### 3.2. 1-Tributylstannyl-1′-heteroarylferrocene (2): general procedure

To the mixture of 1,1′-bis(tributylstannyl)ferrocene (**1**) (2.05 g, 2.68 mmol) and $PdCl_2(PPh_3)_2$ (0.06 g, 0.09 mmol) in dry DMF (6 ml), corresponding bromides (1.78 mmol) were added with stirring. The mixture was heated on an oil bath at 100–120 °C for periods of time given in Table 1. After cooling, saturated ammonium chloride solution was added to the mixture. Then the mixture was extracted with petroleum ether (30–60) or diethyl ether, washed with saturated KF solution and water. The organic layer was dried on $MgSO_4$, filtered, and concentrated in vacuo. 'Flash' chromatography of the crude product was done on neutral or alkaline $Al_2O_3$. The first band eluted with petroleum ether (30–60) was **1** together with some tributylstannylferrocene, then a little destannylation product, ferrocene, was obtained. Continued elution with petroleum ether (30–60)–$Et_2O$ (10:1) gave elutes which yielded the desired product (**2**). The last band was monosbustituted by-product, heterocyclylferrocene.

1-Tributylstannyl-1′-(2-nitro-pyrid-5-yl)ferrocene (**2a**): deep-red oil, 70%. $^1$H-NMR ($CDCl_3$, $\delta$ ppm): 8.66 (d, $J = 2.17$ Hz, 1H), 8.20 (d, $J = 8.22$ Hz, 1H), 7.99 (dd, $J = 2.17$, 8.22 Hz, 1H), 4.75 (m, 2H), 4.49 (m, 2H), 4.21 (m, 2H), 3.96 (m, 2H), 1.78–0.90 (m, 27H). IR ($cm^{-1}$): 3080, 2958, 2927, 2867, 1577, 1533, 1462, 1089,

1024. Anal. Found: C, 54.64; H, 6.67; N, 4.38. Calc. for $C_{27}H_{38}FeN_2O_2Sn$: C, 54.36; H, 6.37; N, 4.69%.

1-Tributylstannyl-1′-(8-methyl-6-nitro-quino-5-yl)-ferrocene (**2b**): deep-red oil, 85%. $^1$H-NMR ($CDCl_3$, $\delta$ ppm): 9.28 (d, $J = 2.16$ Hz, 1H), 8.58 (d, $J = 2.34$, 1H), 8.29 (d, $J = 2.16$ Hz, 1H), 8.19 (d, $J = 2.34$ Hz, 1H), 4.79 (m, 2H), 4.45 (m, 2H), 4.24 (m, 2H), 3.96 (m, 2H), 2.99 (s, 3H), 1.86–0.82 (m, 27H). IR ($cm^{-1}$): 3084, 2958, 2927, 2865, 1612, 1528, 1093, 1026, 435. Anal. Found: C, 60.89; H, 6.23; N, 3.96. Calc. for $C_{32}H_{42}FeN_2O_2Sn$: C, 60.57; H, 6.00; N, 4.00%.

1-Tributylstannyl-1′-(6-methyl-8-nitro-quino-5-yl)-ferrocene (**2c**): deep-red oil, 83%. $^1$H-NMR ($CDCl_3$, $\delta$ ppm): 9.18 (d, $J = 2.08$ Hz, 1H), 8.86 (d, $J = 1.89$ Hz, 1H), 8.03 (d, $J = 2.08$ Hz, 1H), 7.89 (d, $J = 1.89$ Hz, 1H), 4.73 (m, 2H), 4.42 (m, 2H), 4.21 (m, 2H), 3.95 (m, 2H), 2.60 (s, 3H), 1.82–0.80 (m, 27H). IR ($cm^{-1}$): 3043, 2958, 2927, 2865, 1532, 1461, 1085, 1027. Anal. Found: C, 60.83; H, 6.18; N, 3.98. Calc. for $C_{32}H_{42}FeN_2O_2Sn$: C, 60.57; H, 6.00; N, 4.00%.

1-(2-Benzoylthien-5-yl)-1′-(tributylstannyl)ferrocene (**2d**): deep-red oil, 75%. $^1$H-NMR ($CDCl_3$, $\delta$ ppm): 7.92–7.41 (m, 6H), 7.03 (d, $J = 3.92$ Hz, 2H), 4.65 (m, 2H), 4.35 (m, 2H), 4.29 (m, 2H), 3.97 (m, 2H), 1.8–0.9 (m, 27H). IR ($cm^{-1}$): 3084, 2957, 2925, 2863, 1634, 1597, 1514, 1454, 1076, 1025, 1000, 500, 412. Anal. Found: C, 60.10; H, 6.38. Calc. for $C_{33}H_{42}FeOSSn$: C, 59.95; H: 6.36%.

1-Tributylstannyl-1′-(2-acetylthien-5-yl)ferrocene (**2e**): deep-red oil, 65%. $^1$H-NMR ($CDCl_3$, $\delta$ ppm): 7.53 (d, $J = 3.74$ Hz, 1H), 7.50 (d, $J = 3.74$ Hz, 1H), 4.61 (m, 2H), 4.34 (m, 2H), 4.25 (m, 2H), 3.96 (m, 2H), 2.54 (s, 3H), 1.6–0.9 (m, 27H). IR ($cm^{-1}$): 3088, 2958, 2926, 2863, 1653, 1480, 1418, 1080, 1027. Anal. Found: C, 56.26; H, 6.71. Calc. for $C_{28}H_{40}FeOSSn$: C, 56.14; H, 6.68.

### *3.3. 1′,1‴-Bis(heteroaryl)diferrocene (3): general procedure for the homocoupling of 2*

Stoichimetrical amount of $CuSO_4 \cdot 3H_2O$ was added in a single portion to **2** (0.25 mmol) in THF (5 ml). The mixture was stirred at ambient temperature for the time-period given in Table 1. The reaction mixture was diluted with $Et_2O$ (**3d**–**3f**) or $CH_2Cl_2$ (**3a**–**3c**), washed with aqueous ammonia (5% soln.), water, brine, and then dried over $MgSO_4$ and concentrated in vacuo. The crude product was subjected to column chromatography on silica gel (petroleum ether–methanol) and afforded corresponding homocoupling biferrocene derivatives (**3**) in 45–96% yield.

1′,1‴-Bis(2-nitropyrid-5-yl)diferrocene (**3a**): deep-red crystal, 90%, m.p. 158–159 °C. $^1$H-NMR ($CDCl_3$, $\delta$ ppm): 8.74 (s, 2H), 8.17 (d, $J = 8.40$ Hz, 2H), 8.08 (d, $J = 8.40$ Hz, 2H), 4.85 (m, 4H), 4.65 (m, 4H), 4.29 (m, 4H), 4.32 (s, 4H), 4.05 (s, 4H). IR ($cm^{-1}$): 3085, 1577, 1523, 1107, 1081, 1019, 476. MS; $m/z$): 614 ([M], 12).

1′,1‴-Bis(8-methyl-6-nitroquino-3-yl)diferrocene (**3b**): deep-red solid, 85%, m.p. 166 °C (dec.). $^1$H-NMR ($CDCl_3$, $\delta$ ppm): 8.26 (d, $J = 1.84$ Hz, 2H), 8.58 (d, $J = 2.19$ Hz, 2H), 8.25 (m, 4H), 4.87 (s, 4H), 4.51 (s, 4H), 4.32 (s, 4H), 4.10 (s, 4H), 2.90 (s, 6H). IR ($cm^{-1}$): 3113, 1530, 1090, 1028, 475. MS ($m/z$): 742 ([M], 13), 741 (3).

1′,1‴-Bis(6-methyl-8-nitroquino-3-yl)diferrocene (**3c**): deep-red solid, 85%, m.p. 196 °C (dec.). $^1$H-NMR ($CDCl_3$, $\delta$ ppm): 9.21 (bs, 2H), 8.09 (bs, 2H), 7.86 (bs, 2H), 7.78 (bs, 2H), 4.83 (s, 4H), 4.51 (s, 4H), 4.34 (s, 4H), 4.12 (s, 4H), 2.60(s, 6H). IR ($cm^{-1}$): 3085, 1561, 1527, 1090, 1025, 497. MS ($m$/z): 742 ([M], 8).

1′,1‴-Bis(2-benzoylthien-5-yl)diferrocene (**3d**): deep-red solid, 60%, m.p. 128–130 °C. $^1$H-NMR ($CDCl_3$, $\delta$ ppm): 7.90–7.45 (m, 10H), 7.34 (d, $J = 3.93$ Hz, 2H), 6.77 (d, $J = 3.93$ Hz, 2H), 4.45 (bs, 4H), 4.24 (bs, 4H), 4.11 (bs, 10H). IR ($cm^{-1}$): 3064, 1738, 1615, 1465, 1089, 1023, 483. MS ($m/z$): 742 ([M], 20.96), 105 (62.61), 77 (64.62), 56 (19.77).

1′,1‴-Bis(2-acetylthien-5-yl)diferrocene (**3e**): deep-red solid, 45%, m.p. 82–84 °C. $^1$H-NMR ($CDCl_3$, $\delta$ ppm): 7.39 (d, $J = 3.80$ Hz, 2H), 6.71 (d, $J = 3.80$ Hz, 2H), 4.41 (s, 4H), 4.20 (s, 4H), 4.08 (bs, 8H), 2.51 (s, 6H). IR ($cm^{-1}$): 3085, 1698, 1649, 1577, 1458, 1080, 1028, 473. MS ($m/z$): 618 ([M], 16.85), 57 (54), 43 (95.06), 41 (100).

Biferrocene (**3f**): red solid, 96%, m.p. 238 °C (dec.). $^1$H-NMR ($CDCl_3$, $\delta$ ppm): 4.36 (bs, 4H), 4.18 (bs, 4H), 4.01 (s, 10H).

## References


[1] A. Benito, R. Martinez-Manez, J. Paya, J. Sots, M.J.L. Tendero, E. Sinn, J. Organomet. Chem. 503 (1995) 259.
[2] I.R. Butler, J.-L. Roustan, Can. J. Chem. 69 (1991) 1117.
[3] M.-G.A. Shvekhgeimer, Uspekhi Khim. 65 (1996) 43.
[4] S. Nakashima, M. Katada, I. Motoyma, H. Sano, Bull. Chem. Soc. Jpn. 59 (1986) 2923.
[5] M.J. Cohn, T.-Y. Dong, D.N. Hendrickson, S.J. Geib, A.L. Rheingold, J. Chem. Soc. Chem. Commun. (1985) 1059.
[6] S. Iijima, R. Saida, I. Motoyma, H. Sano, Bull. Chem. Soc. Jpn. 54 (1981) 1375.
[7] S. Nakashima, M. Katada, I. Motoyma, H. Sano, Bull Chem. Soc. Jpn. 60 (1987) 2253.
[8] M. Konno, S.-A. Hyodo, S.-I. Iijima, Bull. Chem. Soc. Jpn. 55 (1982) 2327.
[9] R.J. Webb, S.J. Geib, D.L. Staley, A.L. Rheingold, D.N. Hendriekson, J. Am. Chem. Soc. 112 (1990) 5031.
[10] T.-Y. Dong, C.-C. Schei, T.-L. Hsu, S.-L. Lee, S.-J. Li, Inorg. Chem. 31 (1991) 2457.
[11] T.-Y. Dong, C.-K. Chang, C.-H. Huang, Y.-S. Wen, S.-L. Lee, J.-A. Chen, W.-Y. Yeh, A. Yeh, J. Chem. Soc. Chem. Commun. (1992) 526.
[12] T.-Y. Dong, C.-H. Huang, C.-K. Kang, Y.-S. Wen, S.-L. Lee, J.-A. Chen, W.-Y. Yeh, A. Yeh, J. Am. Chem. Soc. 115 (1993) 6357.
[13] T.-Y. Dong, T.-Y. Lee, H.-M. Lin, J Organomet. Chem. 427 (1992) 101.

[14] T.-Y. Dong, C.-C. Schei, M.-Y. Huang, T.-Y. Lee, S.-K. Yeh, Y.-S. Wen, Organometallics 11 (1992) 573.
[15] T.-Y. Dong, T.-J. Ke, S.-M. Peng, S.-K. Yeh, Inorg. Chem. 28 (1998) 2103.
[16] T.-Y. Dong, T.-Y. Lee, S.-H. Lee, G.-H. Lee, S.-M. Peng, Organometallics 13 (1994) 1337.
[17] L.-L. Lai, T.-Y. Dong, J. Chem. Soc. Chem. Commun. (1994) 2347.
[18] T.-Y. Dong, C.-K. Chang, S.-H. Lee, L.-L. Lai, M.Y.-N. Chiang, K.-J. Lin, Organometallics 16 (1997) 5816.
[19] C.-M. Liu, B.-H. Chen, W.-Y. Liu, X.-L. Wu, Y.-X. Ma, J. Organomet. Chem. 598 (2000) 384.
[20] C.-M. Liu, W.-Y. Liu, Y.-M. Liang, Y.-X. Ma, Synth. Commun. 30 (2000) 1755.
[21] C.-M. Liu, Y.-L. Guo, X.-L. Wu, Y.-X. Ma, J. Organomet. Chem. 612 (2000) 172.
[22] M.E. Wright, Organometallics 9 (1990) 853.
[23] T. Sammakia, H.A. Latham, J. Org. Chem. 61 (1996) 1629.
[24] S.-K. Kang, T.-G Baik, X.H. Jiao, Y.-T. Lee, Tetrahedron Lett. 40 (1999) 2383.
[25] R.L. Beddoes, T. Cheeseright, J.Y. Wang, P. Quayle, Tetrahedron Lett. 36 (1995) 283.
[26] E. Piers, E.J. McEachern, M.A. Romero, Tetrahedron Lett. 37 (1996) 1173.