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## Palladium-catalyzed cross-coupling reaction of bis(ferrocenyl)mercury with aryl iodides

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### Abstract

Cross-coupling reactions of bis(ferrocenyl)mercury with aryl- and heteroaryl iodides were shown to be easy and convenient for the synthesis of monoarylsubstituted ferrocenes in high yields. The highly selective substitution of iodine atom in iodobromoarenes by the ferrocenyl unit was demonstrated. © 2000 Elsevier Science Ltd. All rights reserved.

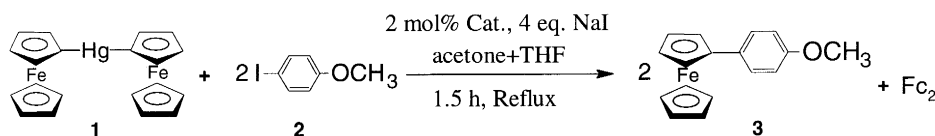
Arylsubstituted ferrocenes attract considerable attention, e.g. for the design of LC materials.<sup>1</sup> Among the numerous ways to obtain arylsubstituted ferrocenes,<sup>2</sup> cross-coupling reactions are the most convenient and productive. Several reports have been published on palladium-catalyzed cross-coupling of iodoferrocene with arylboronic acids<sup>2,3</sup> and organotin compounds,<sup>4</sup> or tin derivatives of ferrocene<sup>5</sup> and ferroceneboronic acids<sup>6</sup> with aryl halides. The problem is that these reactions require preliminary laborious synthesis of iodoferrocene (starting from mercury derivatives of ferrocene),<sup>2</sup> tin or boron derivatives of ferrocene and provide moderate yields of coupling products. Alternatively, zinc derivatives of ferrocene which can be obtained from ferrocene through lithiation by *t*-BuLi, and subsequent reaction with ZnCl<sub>2</sub>, are used in situ in a coupling reaction. Such reactions allow the introduction of a single, as well as several ferrocene fragments into an aromatic ring and give polymeric products in the case of bis(zinc)substituted ferrocenes.<sup>7–10</sup> However, it is hard to expect high selectivity in cross-coupling reactions of ferrocenezinc derivatives with iodobromoarenes and until now there had been no attempt to conduct a coupling of zinc derivatives of ferrocene selectively at the iodine bearing carbon atom in iodobromoarenes. On the other hand, one may suppose that organomercury compounds are more selective, and besides are stable to air and moisture, and are easily obtained by direct mercuration of ferrocene. The purpose of this work is the investigation of the cross-coupling of mercury derivatives of ferrocene with aryl and heteroaryl iodides. One of the main tasks of this work was to find conditions for selective cross-coupling reactions of the ferrocenyl mercury compounds with iodobromoarenes, in order to synthesize bromoarylferrocenes, which can be used in subsequent transformations at the bromine.

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We have found that  $\text{FcHgCl}$  (obtained by direct mercuration of ferrocene)<sup>2</sup> reacts with *p*-iodobromobenzene using  $\text{PdCl}_2(\text{PPh}_3)_2$  as a catalyst and in the presence of potassium iodide in acetone at room temperature (48 h) yielding only a product of iodine substitution, although the yield was low (20%) due to the side reaction of homocoupling (yield of bis(ferrocenyl) ( $\text{Fc}_2$ ) was also about 20%). Since we observed the transformation of  $\text{FcHgCl}$  into bis(ferrocenyl)mercury in the presence of iodide anion in the course of the reaction, we investigated a cross-coupling of  $\text{Fc}_2\text{Hg}$  (**1**) with *p*-iodobromobenzene. We found a higher conversion of starting compounds and observed a higher yield (72%) of 4- $\text{BrC}_6\text{H}_4\text{Fc}$  under the same conditions in the THF:acetone (3:2) mixture. Bis(ferrocenyl) (11%) and 1,4-bis(ferrocenyl)benzene (8%) were also found in the products. It should be noted that both ferrocene fragments of (**1**) were involved in the reactions.

A similar result was observed for the reaction of  $\text{Fc}_2\text{Hg}$  with 4,4'-iodobromobiphenyl under the same conditions. Heating allowed the reaction time to be shortened to 1.5 h, increasing the conversion of  $\text{Fc}_2\text{Hg}$  to 100% and the yield of 4- $\text{BrC}_6\text{H}_4\text{Fc}$  to 88% ( $\text{Fc}_2$  was not detected, although 10% of the product of bis-coupling was formed).

It was demonstrated that aryl iodides with electron-withdrawing substituents react better than those with electron-donating substituents. We investigated the influence of the nature of the catalyst on the result of the cross-coupling reaction of  $\text{Fc}_2\text{Hg}$  with *p*-iodoanisole (**2**), which initially showed the poorest yields in the cross-coupling reaction in presence of  $\text{PdCl}_2(\text{PPh}_3)_2$  (Scheme 1). The results are presented in Table 1.



Scheme 1.

Table 1

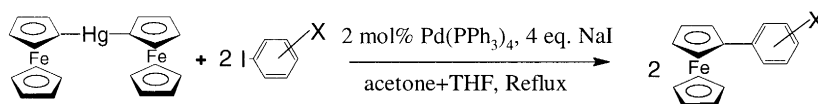
Influence of the catalyst on the yield of cross-coupling reaction of  $\text{Fc}_2\text{Hg}$  with *p*-iodoanisole

No	Catalyst	conversion at $\text{Fc}_2\text{Hg}$	$\text{Fc}_2$ / <b>3</b>	Yield <sup>a</sup> , %	Yield <sup>b</sup> , %
1	$\text{PdCl}_2(\text{PPh}_3)_2$	100	1 / 2.1	67	67 (66)
2	$\text{PdCl}_2(\text{dppf})$	70	5.3 / 1	13	9
3	$\text{PdCl}_2(\text{L})^c$	66	2.5 / 1	27	18
4	$\text{PdCl}_2(\text{MeCN})_2$	58	3.3 / 1	22	12
5	$\text{Pd}(\text{PPh}_3)_4$	100	1 / 9	80	80 (80)

<sup>a</sup>Yield is based on the amount of reacted  $\text{Fc}_2\text{Hg}$ . <sup>b</sup>Yield is based on the amount of  $\text{Fc}_2\text{Hg}$  as starting material (isolated yields are presented in brackets). <sup>c</sup>L = 2,2'-bis(diphenylphosphino)diphenyl ether

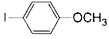
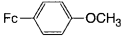
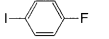
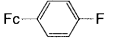
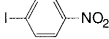
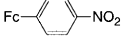
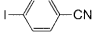
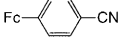
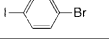
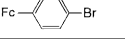
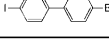
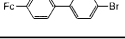
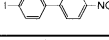
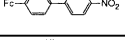
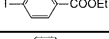
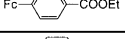
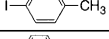
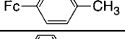
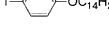
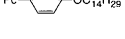
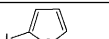
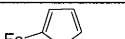
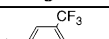
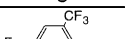
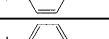
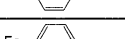
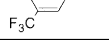
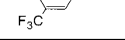
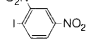
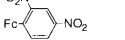
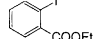
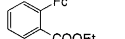
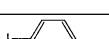

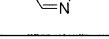
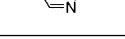
Complexes of  $\text{PdCl}_2$  with dppf, 2,2'-bis(diphenylphosphino)diphenyl ether and acetonitrile were less effective than  $\text{PdCl}_2(\text{PPh}_3)_2$  and yielded bis(ferrocenyl) as the main product with low conversion. The best result was obtained with  $\text{Pd}(\text{PPh}_3)_4$  (entry 5)—80% of product of cross-coupling with 100% conversion of  $\text{Fc}_2\text{Hg}$ .

Further, we have conducted coupling reactions of bis(ferrocenyl)mercury with different aryl (heteroaryl) iodides under these conditions (Scheme 2). The results are shown in Table 2.



Scheme 2.

Table 2  
Yields of arylferrocenes from cross-coupling of  $\text{Fc}_2\text{Hg}$  with iodoarenes

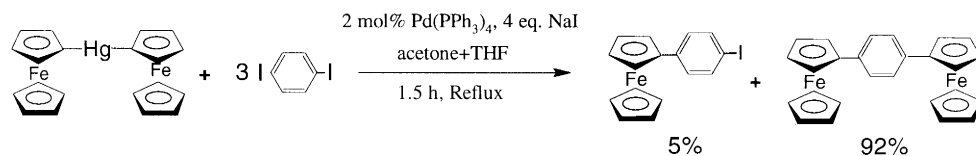
No	ArI	time h	cross-coupling products	Yield, % on NMR (isolated)	NMR $^1\text{H}$ in $\text{CDCl}_3$ ( $\delta$ , p.p.m.)	mp. $^\circ\text{C}$
1		1.5		80 (80)	7.38 (2 H, m), 6.83 (2 H, m), 4.56 (2H, m), 4.25 (2H, m), 4.02 (5H, s), 3.80 (3H, s).	106-107 (113) <sup>2</sup>
2		1.5		94 (92)	7.42 (2 H, m), 6.97 (2 H, m), 4.57 (2H, m), 4.28 (2H, m), 4.02 (5H, s).	106 (104) <sup>2</sup>
3 <sup>a</sup>		1		98 (96)	8.12 (2 H, m), 7.54 (2 H, m), 4.73 (2H, m), 4.46(2H, m), 4.04 (5H, s).	171 (169-170) <sup>11</sup>
4 <sup>a</sup>		1.5		97 (97)	7.52 (4 H, m), 4.68 (2H, m), 4.41 (2H, m), 4.03 (5H, s).	141-142 (145-146) <sup>11</sup>
5		1.5		88 (88)	7.58 (2 H, m), 7.32 (2 H, m), 4.59 (2H, m), 4.31 (2H, m), 4.02 (5H, s).	124 (122-123) <sup>11</sup>
6		1.5		89 (88)	7.53 (4 H, m), 7.46 (4 H, m), 4.66 (2H, m), 4.33 (2H, m), 4.05 (5H, s).	199 (200-201) <sup>14</sup>
7		1.5		98 (95)	7.74 (2 H, m), 7.55 (4 H, m), 7.28 (2 H, m), 4.70 (2H, m), 4.37 (2H, m), 4.06 (5H, s).	224-225
8		1.5		98 (97)	7.94 (2 H, m), 7.48 (2 H, m), 4.71 (2H, m), 4.38 (2H, m), 4.36 (2H, q), 4.03 (5H, s), 1.39 (3H, t).	92-93 (88-90) <sup>11</sup>
9		1.5		93 (90)	7.36 (2 H, m), 7.08 (2 H, m), 4.59 (2H, m), 4.26 (2H, m), 4.01 (5H, s), 2.31 (3H, s).	136-138 (140-142) <sup>11</sup>
10		1.5		85 (84)	7.37 (2 H, m), 6.82 (2 H, m), 4.54 (2H, m), 4.24 (2H, m), 4.01 (5H, s), 3.94 (2H, t), 1.78 (2H, m), 1.43 (2H, m), 1.25 (20H, m), 0.87 (3H, t).	93
11		1.5		94 (90)	7.13 (1 H, m), 6.98 (1 H, m), 6.90 (1 H, m), 4.55 (2H, m), 4.25 (2H, m), 4.07 (5H, s).	121-122 (116-118) <sup>12</sup>
12		1.5		97 (96)	7.64 (2 H, m), 7.39 (2 H, m), 4.66 (2H, m), 4.35 (2H, m), 4.03 (5H, s).	96 (97.5-98) <sup>11</sup>
13		28		62 (60)	8.03 (1 H, m), 7.58 (1 H, m), 7.49 (1 H, m), 7.30 (1 H, m), 4.55 (2H, m), 4.30 (2H, m), 4.14 (5H, s).	52 (80-82) <sup>13</sup>
14		1.5		91 (87)	8.32 (1 H, m), 8.27 (1 H, m), 7.91 (1 H, m), 4.58 (2H, m), 4.52 (2H, m), 4.12 (5H, s).	162
15		20		87 (85)	7.79 (1 H, m), 7.47 (1 H, m), 7.40 (1 H, m), 7.23 (1 H, m), 4.44 (2H, m), 4.26 (2H, m), 4.17 (2H, q), 4.07(5H, s), 1.17 (3H, t).	51-52
16 <sup>a</sup>		1.5		84 (84)	8.74 (1 H, m), 8.42 (1 H, m), 7.72 (1 H, m), 7.21 (1 H, m), 4.66 (2H, m), 4.37 (2H, m), 4.05 (5H, s).	57 (57-59) <sup>15</sup>
17 <sup>b</sup>		1.5		92	7.38 (4 H, s), 4.63 (4H, m), 4.30 (4H, m), 4.04 (10H, s).	
18 <sup>b</sup>		1.5		24	7.34 (2 H, m), 6.76 (2 H, m), 4.84(1H, s), 4.54 (2H, m), 4.25 (2H, m), 4.02 (5H, s).	(162) <sup>2</sup>

<sup>a</sup>  $\text{PdCl}_2(\text{PPh}_3)_2$  was used as a catalyst; <sup>b</sup> the product was not isolated.

We found that in the presence of  $\text{Pd}(\text{PPh}_3)_4$  bis(ferrocenyl)mercury provided almost quantitative yields in cross-coupling with different aryl iodides and demonstrate high selectivity in cross-coupling reactions with iodobromoarenes (entries 5 and 6). However, 4-iodophenol was an exception as we failed to obtain yields higher than 24%. The introduction of substituent in the *ortho*-position of the aryl iodide considerably increased the time of reaction and decreased the yield (with the exception of 2,4-dinitroiodobenzene). The reaction with 1,4-diiodobenzene led to the product of double substitution in a high yield (92%) (even if 50% excess of 1,4-diiodobenzene was used) (Scheme 3).

All compounds obtained were characterised by  $^1\text{H}$  NMR spectra. Correct element analysis data for the new compounds have been received.

In a typical experiment 0.12 mmol  $\text{Fc}_2\text{Hg}$ , 0.28 mmol iodoarene, 0.48 mmol NaI, 3 ml freshly distilled THF and 2 ml dry acetone were refluxed under argon with 4.8  $\mu\text{mol}$  (2 mol%) of a catalyst. The reaction



Scheme 3.

was monitored by TLC. After the reaction was finished (Table 2), the mixture was filtered through silica gel, evaporated in vacuo, and purified by column chromatography using silica gel (benzene–hexane).

## Acknowledgements

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