

## A CONVENIENT PREPARATION OF IODOFERROCENES

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**Abstract**—The synthesis of iodoferrocenes using stannylferrocenes as key intermediates is described. The method is suitable for the bulk preparation of iodoferrocenes.

There has been a definite resurgence in the chemistry of metallocenes and in particular ferrocene chemistry in the past year or so. This comes with the recognition that ferrocene may be a useful synthon in the rapidly expanding areas of "new material science", for example in molecular ferromagnets,<sup>1,2</sup> molecular sensors<sup>3,4</sup> and self assembly.<sup>5-7</sup>

A significant proportion of ferrocene-based synthetic work relies on a few key reagents such as lithio-ferrocenes,<sup>8,9</sup> ferrocenylcarboxaldehydes,<sup>10,11</sup> ferrocenylcarboxylic acids<sup>12</sup> and haloferrocenes.<sup>12-14</sup> The conventional synthesis of haloferrocenes has been via either ferrocenylmercury reagents<sup>15-17</sup> or ferrocenyl boronic acids,<sup>18</sup> or the direct reaction of lithioferrocenes with hexachloroethane,<sup>19</sup> tetrabromodichloroethane or iodine<sup>20</sup> (Scheme 1). We have made use of these synthetic procedures for several years and have found them to be satisfactory; however, yields of iodoferrocenes tend to be low and variable. In one of our current research projects we require large quantities of iodoferrocene and, therefore, we decided to look for an alternative synthesis which would give more predictable and higher yields and at the same time be economically acceptable. A reasonable route seemed to be via organo-tin compounds since the halogen/organotin exchange reaction is well established. Wright has published the synthesis and use of 1,1'-bis-(tri-n-

butylstannyl)ferrocene and its use as a precursor to monolithioferrocenes:<sup>21</sup> this reagent seemed well suited as a synthetic intermediate since the precursors required are inexpensive.

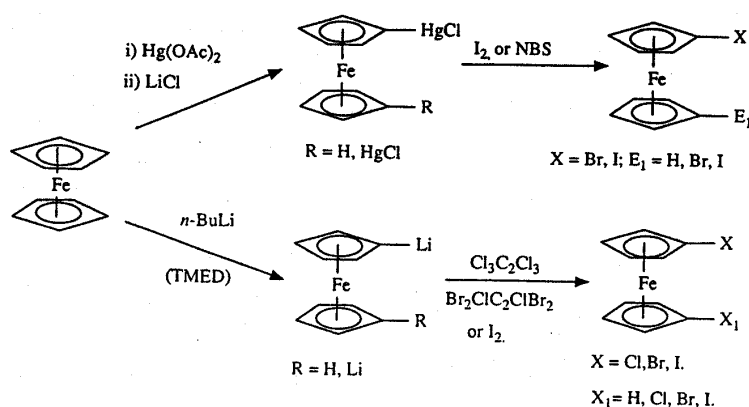
### EXPERIMENTAL

Bis-tri-n-butylstannylferrocene (BSSF) or tri-n-butylstannylferrocene (BSF) were prepared by the literature procedure and purified by repeated chromatography on a neutral alumina support where pure samples were required. In some experiments crude BSSF and BSF were used, which had been purified by one chromatographic separation only. Bis-triphenylstannylferrocenes and triphenylstannylferrocene were prepared by reaction of dilithioferrocene or monolithioferrocene, respectively, with chlorotriphenyltin and were crystallized prior to use.

#### *Reaction of crude BSF or BSSF with I<sub>2</sub>*

A cooled (approx -70°C) sample of either crude (isolated without column chromatography) BSF or BSSF (0.25 mol) in dichloromethane (1000 cm<sup>3</sup>) was treated with I<sub>2</sub> (0.27 mol or 0.54 mol I<sub>2</sub>, respectively) under a nitrogen atmosphere. The mixture was allowed to warm to room temperature and was stirred overnight. The mixture was then washed twice with 1 M solutions of sodium thiosulphate (200 cm<sup>3</sup>), the organic layer separated and flashed through a small portion of neutral alumina. The

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solvent was then removed on a rotary evaporator to leave a viscous oil which was dissolved in MeOH (1000 cm<sup>3</sup>). Excess KF (50 g) was then added to precipitate the stannyl by-products. The precipitated material was removed by filtration and the MeOH was removed *in vacuo*. The solid/oil was then extracted with several portions of diethyl ether, again flashed through an alumina plug and the solvent removed to give an amber oil. <sup>1</sup>H NMR indicated the product iodo- or di-iodoferrocene was in each case contaminated with butyl-tin derivatives. Further separation and isolation of the iodo- or di-iodoferrocene were attempted but found to be extremely difficult except on small scale chromatographic purifications on neutral alumina.

#### Reaction of pure BSF or BSSF with I<sub>2</sub> or ICl

Identical reactions to the above method were carried out using pure bis-tri-*n*-butylstannylferrocene or tri-*n*-butylstannylferrocene on scales of up to 100 g of the starting compounds. These yielded pure 1,1'-di-iodo- or iodoferrocene, respectively, as amber oils without the need for chromatography. Yields are > 80% on average.

An identical reaction procedure using ICl in place of I<sub>2</sub> gave higher yields (> 90%) of the appropriate iodoferrocene.

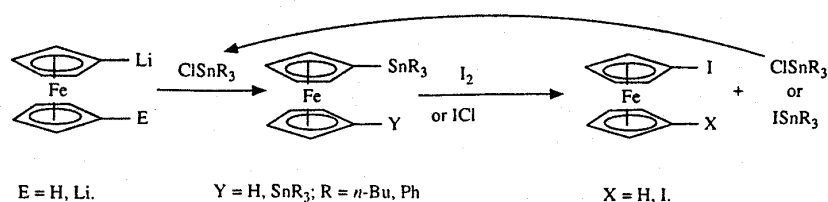
#### Reaction of pure triphenylstannylferrocenes with ICl

The reaction of bis-triphenylstannylferrocene with ICl on a 0.2 mol scale gave bis 1,1'-diiodoferrocene as the sole ferrocene containing product. A similar methodology to the above was used except that it is not necessary to use KF since the by-products are not soluble in weakly polar solvents. For the work-up the solvent was removed from the crude reaction mixture and the product di-iodo-

ferrocene was extracted into the diethyl ether and purified by passing the yellow product solution through an alumina plug. The yields using this procedure were > 85%. Similar treatment of triphenylstannylferrocene with ICl gave iodoferrocene again in high yield.

## RESULTS AND DISCUSSION

The syntheses of tri-*n*-butylstannylferrocene (BSF) and 1,1'-bis-*n*-(tri-*n*-butylstannyl)ferrocene (BSSF) are straightforward.<sup>21</sup> The compounds are prepared from lithioferrocenes by reaction with tri-*n*-butylstannyl chloride and are obtained as golden brown oils. Purification of the product compounds is effected using column chromatography on a neutral alumina support, using hexane as an eluent. In the case of BSSF synthesis when the reactions were scaled up (> 50 g) the chromatographic purification became more difficult unless extremely large quantities of alumina were used. The ferrocene and BSF were easily removed from the BSSF; however, tetrabutyltin was more difficult to remove on a large scale. On treatment of pure BSSF with I<sub>2</sub> or ICl the 1,1'-di-iodoferrocene cleanly forms in near quantitative yield and thus provides a viable alternative route for the synthesis of di-iodoferrocene. The product iodoferrocenes are isolated by removal of the co-produced stannyl chlorides or iodides. This was achieved by treatment of the crude reaction mixtures with KF in methanol, followed by filtration to remove the precipitated tri-*n*-butylstannylfluoride. Since it would be advantageous to use crude BSF or BSSF, attempts were made to use unchromatographed samples arising directly from the reaction of lithioferrocenes with tri-*n*-butylstannyl chloride. However, the actual isolation of the product posed problems, especially when carried out on a large scale (> 50 g). The problem



Scheme 2.

arises from residual impurities such as tetrabutyltin (formed by reaction of butyllithium with the tributylstannyl chloride) without several chromatographic steps.<sup>22</sup> Therefore, it is important to use pure 1,1'-bis-tri-*n*-butylstannylferrocene as the starting compound and not to proceed with an impure mixture—the best check of sample purity (BBSF or BSF) is to use the integration of the <sup>1</sup>H NMR cyclopentadienyl signals versus those of the butyl resonances as the basis for evaluation. Using pure 1,1'-bis-tri-*n*-butyl stannylferrocene we have been able to prepare > 100 g quantities of di-iodoferrocene in one batch. The drawback is that the alumina required for purification of the stannylferrocenes is now rather expensive. We therefore decided to examine the use of tri-phenylstannylferrocenes, which are solids and are easily purified by crystallization. Using the same methodology we have found that di-iodoferrocene is readily obtained in the same manner without the problems caused by impurities. The drawback here, however, is that chlorotriphenyltin is more commercially expensive than the butyl compound so that may limit large scale application.

In principle, the halo-stannyl by-products could be recycled (Scheme 2, step 1). We are currently attempting modifications to the isolation procedure which would allow this. Small scale experiments indicate that the procedure is applicable to the synthesis of bromoferrocenes; however, the yields are considerably diminished presumably caused by the direct side-reaction of bromine with ferrocene.

## REFERENCES

1. C. Kollmar, M. Couty and O. Kahn, *J. Am. Chem. Soc.* 1991, **113**, 7994.
2. K. M. Chi, J. C. Calbrese, W. M. Reiff and J. S. Miller, *Organometallics* 1991, **10**, 668.
3. R. W. Wagner, P. A. Brown, T. E. Johnson and J. S. Lindsey, *J. Chem. Soc., Chem. Commun.* 1991, 1463.
4. E. C. Constable, *Angew. Chem., Int. Edn Engl.* 1991, **30**, 407.
5. J. C. Medina, C. Li, S. G. Bott, J. L. Atwood and G. W. Gokel, *J. Am. Chem. Soc.* 1991, **113**, 366.
6. M. C. Grossel, M. R. Goldspink, J. A. Hrijac and S. C. Weston, *Organometallics* 1991, **10**, 851.
7. P. D. Beer, E. L. Tite and A. Ibbotson, *J. Chem. Soc., Dalton Trans.* 1991, 1691.
8. M. D. Rausch and D. J. Clappenelli, *J. Organomet. Chem.* 1967, **10**, 127.
9. M. D. Rausch, G. A. Moser and C. F. Meade, *J. Organomet. Chem.* 1973, **51**, 1.
10. P. L. Pauson and W. E. Watts, *J. Chem. Soc.* 1962, 3880.
11. J. M. Osgerby and P. L. Pauson, *J. Chem. Soc.* 1961, 4604.
12. P. C. Reeves, *Org. Synth.* 1970, **56**, 28.
13. M. D. Rausch, L. P. Klemann, A. Siegel, R. F. Kovar and T. M. Gund, *Synth. Inorg. Met.-Org. Chem.* 1973, **3**, 193.
14. A. N. Nesmeyanov, E. G. Perevalova and A. N. Nesmeyanov, *Dokl. Akad. Nauk., SSSR* 1955, **100**, 1099.
15. R. W. Fish and M. Rosenblum, *J. Org. Chem.* 1965, **30**, 1253.
16. A. N. Nesmeyanov, E. G. Perevalova, R. A. Golovnya and O. A. Nesmeyanov, *Dokl. Akad. Nauk., SSSR* 1954, **97**, 459.
17. *Handbuch der Anorg. Chem.*, 8th edn. Suppl. **14**, A368. Gmelin (1974).
18. H. Shechter and J. F. Helling, *J. Org. Chem.* 1961, **26**, 1034.
19. F. L. Hedberg and H. Rosenberg, *J. Am. Chem. Soc.* 1973, **95**, 870.
20. For a series of general references see *Organometallic Compounds of Iron* (Edited by G. Knox). Chapman and Hall, New York (1985).
21. M. E. Wright, *Organometallics* 1990, **9**, 853.
22. It is very difficult to remove tetrabutyltin from the product iodoferrocenes without repeated rigorous chromatography on small sample quantities. If only slight quantities are present, however, in the case of iodoferrocene synthesis, the iodoferrocene can be successfully crystallized at low temperatures.