Journal of Organometallic Chemistry 853 (2017) 74–80

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Mercuration of ferrocenyl-*p*-tolyl sulfoxide and its conversion to 1,2-disubstituted ferrocenes

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ARTICLE INFO

Article history:
Received 2 August 2017
Received in revised form
18 October 2017
Accepted 19 October 2017
Available online 21 October 2017

Keywords:
Cyclomercurated ferrocene
1,2-disubstituted ferrocene
p-tolylsulfinyl ferrocene

ABSTRACT

1-(*p*-Tolylsulfinyl)-2-(chloromercurio)ferrocene (**2**) was prepared by direct mercuration of ferrocenylsulfoxide (**1**). This reaction can be performed at room temperature in open air. Cross-coupling reactions of compound **2** and aryl halides especially aryl iodides resulted in 1,2-disubstituted ferrocene derivatives with moderate to good yields.

1. Introduction

Ferrocene and its derivatives are of great interest in the fields of materials science, catalysis, biomedical research and so on [1–3]. The interest in ferrocene continues to grow owing to its versatility in the synthesis of numerous derivatives, reversible redox properties and thermal stability [4–6]. Different approaches have been utilized to make 1,1′ (or) 1,2 (or) 1,3-disubstituted ferrocenes. Among the different disubstituted ferrocenes, 1,2-disubstiuted ferrocenes have gained interest, since the pioneering work of Ugi's diastereoselective generation of planar chirality [7]. *ortho*-Metallation introduced by different chiral auxiliaries such as oxazolines [8,9], hydrazones [10,11], sulfoxides [12], sulfoximines [13], pyrrolidines [14], and acetals [15,16] have been most widely used as the synthetic tool to make 1,2-disubstituted ferrocenes.

The sulfoxide methodology introduced by Kagan and co-workers has the advantage to act as (1) an excellent diastereoselective *ortho*-directing group to make planar chiral compounds, (2) the sulfoxide group can be replaced by different substituents to make 1,2-disubstituted compounds and (3) the absolute configuration of the resultant 1,2-substituted ferrocenes are always predictable [12]. However most of the achiral and chiral 1,2-disubstituted ferrocenes synthesized using this methodology involved organo lithium reagents for the deprotonation of the *ortho*-position of the ferrocenyl ring [16–24]. Here we report the synthesis of 1-(aryl)-2-(*p*-tolylsulfinyl)ferrocenes using direct mercuration of ferrocenyl *p*-tolyl sulfoxide followed by palladium-catalyzed cross-coupling of 1-(*p*-tolylsulfinyl)-2-(chloromercurio) ferrocene and aryl halides especially aryl iodides.

2. Experimental

2.1. Synthesis

2.1.1. General

All chemicals were used as received from commercially available sources. DL-menthol, ferrocene, $^{t}Bu_3SnCl$ were procured from Sigma-Aldrich. All solvents were purified and dried according to standard procedures. Ferrocenyl *p*-tolyl sulfoxide was prepared according to literature procedure using menthyl-*p*-toluenesulfinate prepared from DL-menthol [16,17]. NMR spectra were recorded on Bruker 700 and ARX 400 spectrometers at room temperature. ^{1}H (700 MHz), ^{13}C (176 MHz), ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR chemical shifts in ppm were referenced internally to its proton resonance of incomplete deuterated solvent signals. In case of compounds **2**, **3c**, **3d** & **3h** the splitting for Cp protons were not observed due to fluxional behavior of the sulfoxide. Electrospray ionization (ESI) mass spectra were recorded on a Bruker microTOF-

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https://doi.org/10.1016/j.jorganchem.2017.10.028
0022-328X/

QII spectrometer. Single crystal X-ray diffraction data were collected on a Bruker APEX-II diffractometer. The data were collected at 296 K using, Mo-Kα radiation (0.71073 Å). Crystallographic data for **2, 3a, & 5** and details of X-ray diffraction experiments and crystal structure refinements are given in Table S1. Using Olex2, the structures were solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms were placed at calculated positions and were refined as riding atoms. Crystallographic data for the structures of **2, 3a, & 5** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1565373, 1565374, 1526742. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk): (*Caution*: Organomercurials are highly toxic, hence appropriate handling should be followed for their generation and disposal).

2.1.2. Synthesis of 1-(p-tolylsulfinyl)-2-(chloromercurio)ferrocene (2)

Ferrocenyl *p*-tolyl sulfoxide (**1**) (0.32 g, 1.0 mmol) was dissolved in 5 mL of dichloromethane, in 100 mL two necked round bottom flask fitted with a magnetic stirrer and an equilibrated addition funnel. $Hg(OAc)_2$ (0.32 g, 1.0 mmol) was dissolved in a sufficient amount of MeOH. This solution was added dropwise to compound **1**, over a period of 25 min in open air. Then, 0.08 g of LiCl (2.0 mmol) dissolved in MeOH, was added through addition flask over 20 min and the stirring was continued for 24 h. Finally the solvents were evaporated under reduced pressure and the resulting crude mixture was dissolved in dichloromethane (10 mL), filtered through frit to remove the insoluble salts. The solution was transferred to a separating funnel, then 50 mL of water was added. The organic layer was separated and the process was repeated twice. The collected organic fractions were dried over Na_2SO_4. The resulting solution was evaporated *in vacuo* and subjected to a flash column chromatography on silica gel, eluted with *n*-hexane/ethylacetate (4:1 ratio). The first band was collected and afforded the title compound **2** in 40% yield (0.22 g, 0.4 mmol). The crude yellow solid was recrystallized from dichloromethane and *n*-hexane 1:0.2 ratio to afford the corresponding compound **2** as a reddish yellow crystals. mp = 159–160 °C. ^{1}H NMR (700 MHz, Benzene-d_6) δ = 7.38 (d, J = 7.9 Hz, 2H, ArH), 6.76 (d, J = 7.9 Hz, 2H, ArH), 4.32 (s, 1H, Cp), 4.05 (s, 5H, Cp), 3.96 (s, 1H, Cp), 3.62 (s, 1H, Cp), 1.86 (s, 3H, CH_3). ^{13}C NMR (176 MHz, Benzene-d_6) δ = 144.9, 141.1, 130.3, 123.9, 99.6 (Cp), 76.6 (Cp), 75.1 (Cp), 73.0 (Cp), 70.8 (Cp), 69.0 (Cp), 21.2(CH_3). HR-MS (ESI): calcd. for $C_{17}H_{15}ClFeHgSO$ ($[M]^+$): 559.9656, found: 559.9628.

2.1.3. General procedure: Cross-coupling reaction between 1-(p-tolylsulfinyl)-2-(chloromercurio)ferrocene and electrophiles catalyzed by Pd(0)

In a Schlenk tube 0.5 mmol of compound **2**, 1.25 mmol of ArI, 2.0 mmol of NaI and $Pd(PPh_3)_4$ (2 mol %) were placed. Subsequently, 3 mL of dry THF and 2 mL of dry acetone were added and the reaction mixture was refluxed for the time mentioned in the procedure. The reaction mixture was filtered through a pad of silica, washed with 2 × 20 mL of THF and the resultant filtrate was concentrated. The crude product was purified by flash column chromatography using *n*-hexane and ethyl acetate as an eluent to afford the desired 1,2-disubstituted ferrocenyl product.

2.1.4. 1,2-disubstituted p-tolylsulfinyl ferrocene derivatives

1-(4-Cyanophenyl)-2-(*p*-tolylsulfinyl)ferrocene (**3a**): The quantities involved are as follows. Compound **2** (0.200 g, 0.36 mmol), 4-iodobenzonitrile (0.204 g, 0.89 mmol), sodium iodide (0.214 g, 1.43 mmol) and $Pd(PPh_3)_4$ (0.012 g, 2.0 mol %). After refluxing for 2 h the title compound was purified by flash column chromatography (*n*-hexane: EtOAc 4:1). Yield = 0.138 g (90%), mp = 189–190 °C. ^{1}H NMR (700 MHz, Benzene-d_6) δ = 7.69 (d, J = 7.0 Hz, 2H, ArH), 7.44 (d, J = 7.0 Hz, 2H, ArH), 7.01 (d, J = 7.0 Hz, 2H, ArH), 6.73 (d, J = 7.0 Hz, 2H, ArH), 4.22 (dd, J = 2.7, 1.6 Hz, 1H, Cp), 4.15 (dd, J = 2.6, 1.6 Hz, 1H, Cp), 4.00 (s, 5H, Cp), 3.95 (t, J = 2.6 Hz, 1H, Cp), 1.85 (s, 3H, CH_3). ^{13}C NMR (176 MHz, Benzene-d_6) δ = 142.7, 142.2, 141.1, 132.2, 131.0, 129.9, 125.8, 119.6, 111.4, 95.5 (Cp), 86.6 (Cp), 73.6 (Cp), 72.4 (Cp), 72.3 (Cp), 70.3 (Cp), 21.5 (CH_3). HR-MS (ESI): calcd. for $C_{23}H_{19}FeNOS$ ($[M+H]^+$): 426.0610, found: 426.0635.

Synthesis of 1-(4-cyanophenyl)-2-(*p*-tolylsulfinyl)ferrocene (**3a**) from 4-bromobenzonitrile: The quantities involved are as follows. Compound **2** (0.150 g, 0.27 mmol), 4-bromobenzonitrile (0.122 g, 0.67 mmol), sodium iodide (0.161 g, 1.07 mmol) and $Pd(PPh_3)_4$ (0.006 g, 2.0 mol%). After refluxing for 2 h the title compound was purified by flash column chromatography (*n*-hexane: EtOAc 4:1). Yield = 0.055 g (48%).

1-(Phenyl)-2-(*p*-tolylsulfinyl)ferrocene (**3b**): The quantities involved are as follows. Compound **2** (0.200 g, 0.36 mmol), iodobenzene (0.182 g, 0.89 mmol), sodium iodide (0.214 g, 1.43 mmol) and $Pd(PPh_3)_4$ (0.009 g, 2.0 mol %). After refluxing for 12 h the title compound was purified by flash column chromatography (*n*-hexane:EtOAc 4:1). Yield = 0.110 g (76%), mp = 163–164 °C. ^{1}H NMR (700 MHz, Benzene-d_6) δ = 8.01 (m, 2H, ArH), 7.63 (d, J = 8.1 Hz, 2H, ArH), 7.18 (d, J = 8.1 Hz, 2H, ArH), 7.06 (m, 1H, ArH), 6.79 (d, J = 8.1 Hz, 2H, ArH), 4.37 (dd, J = 2.6, 1.5 Hz, 1H, Cp), 4.12 (dd, J = 2.7, 1.5 Hz, 1H, Cp), 4.01 (s, 5H, Cp), 3.96 (t, J = 2.6 Hz, 1H, Cp), 1.91 (s, 3H, CH_3). ^{13}C NMR (176 MHz, Benzene-d6) δ = 142.6, 140.9, 137.3, 131.0, 129.8, 128.9, 127.9, 126.3, 94.6 (Cp), 90.0 (Cp), 72.6 (Cp), 72.1 (Cp), 71.7 (Cp), 69.6 (Cp), 21.6 (CH_3). HR-MS (ESI): calcd. for $C_{23}H_{20}FeOS$ ($[M+H]^+$): 401.0657, found: 401.0672.

Synthesis of 1-(phenyl)-2-(*p*-tolylsulfinyl)ferrocene (**3b**) from bromobenzene: The quantities involved are as follows. Compound **2** (0.150 g, 0.27 mmol), bromobenzene (0.105 g, 0.67 mmol), sodium iodide (0.161 g, 1.07 mmol) and $Pd(PPh_3)_4$ (0.006 g, 2.0 mol%). After refluxing for 12 h the title compound was not observed.

1-(4-Florophenyl)-2-(*p*-tolylsulfinyl)ferrocene (**3c**): The quantities involved are as follows. Compound **2** (0.280 g, 0.5 mmol), 1-fluoro-4-iodobenzene (0.280 g, 1.25 mmol), sodium iodide (0.300 g, 2.0 mmol) and $Pd(PPh_3)_4$ (0.012 g, 2.0 mol%). After refluxing for 4 h the title compound was purified by flash column chromatography (*n*-hexane: EtOAc 4:1). Yield = 0.160 g (76%), mp = 148–149 °C. ^{1}H NMR (700 MHz, Benzene-d_6) δ = 7.80 (d, J = 8.4 Hz, 2H, ArH), 7.54 (d, J = 7.7 Hz, 2H, ArH), 6.80 (d, J = 8.4 Hz, 2H, ArH), 6.76 (d, J = 7.7 Hz, 2H, ArH), 4.24 (s, 1H, Cp), 4.15 (s, 1H, Cp), 4.03 (s, 5H, Cp), 3.94 (s, 1H, Cp), 1.88 (s, 3H, CH_3). ^{13}C NMR (176 MHz, Benzene-d_6) δ = 163.7 (d, J = 246 Hz), 142.5, 140.9, 133.2 (d, J = 3 Hz), 132.7 (d, J = 8 Hz), 129.8, 126.3, 126.0, 115.5 (d, J = 21 Hz), 94.6 (Cp), 88.8 (Cp), 72.4 (Cp), 72.1 (Cp), 72.1 (Cp), 69.5 (Cp), 21.6 (CH_3). HR-MS (ESI): calcd. for $C_{23}H_{19}FFeOS$ ($[M+H]^+$): 419.6452, found: 419.6469.

1-(4-Bromophenyl)-2-(*p*-tolylsulfinyl)ferrocene (**3d**): The quantities involved are as follows. Compound **2** (0.400 g, 0.72 mmol), 1-bromo-4-iodobenzene (0.484 g, 1.78 mmol), sodium iodide (0.430 g, 2.86 mmol) and $Pd(PPh_3)_4$ (0.017 g, 2.0 mol %). After refluxing for 4 h the title compound was purified by flash column chromatography (hexane: EtOAc 4:1). Yield = 0.291 g (85%), mp = 155–156 °C. ^{1}H NMR (700 MHz, Benzene-d_6) δ = 7.69 (d, J = 8.0 Hz, 2H, ArH), 7.53 (d, J = 7.8 Hz, 2H, ArH), 7.25 (d, J = 8.0 Hz, 2H, ArH), 6.75 (d, J = 7.8 Hz, 2H, ArH), 4.21 (s, 1H, Cp), 4.16 (s, 1H, Cp), 4.01 (s, 5H, Cp), 3.93 (s, 1H, Cp), 1.87 (s, 3H, CH_3). ^{13}C NMR (176 MHz, Benzene-d_6) δ = 141.6, 140.2, 135.7, 131.7, 131.0, 129.0, 125.2, 121.0, 94.0 (Cp), 87.3 (Cp), 71.6 (Cp), 71.4 (Cp), 71.3 (Cp), 68.9

(Cp), 20.7 (CH_3). HR-MS (ESI): calcd. for $C_{23}H_{19}BrFeOS$ ($[M+H]^+$): 478.9764, found: 478.9791.

1-(4-Trifluoromethylphenyl)-2-(*p*-tolylsulfinyl)ferrocene (**3e**): The quantities involved are as follows. Compound **2** (0.200 g, 0.36 mmol), 4-iodobenzotrifluoride (0.240 g, 0.89 mmol), sodium iodide (0.214 g, 1.43 mmol) and $Pd(PPh_3)_4$ (0.012 g, 2.0 mol%). After refluxing for 4 h the title compound was purified by flash column chromatography (*n*-hexane: EtOAc 4:1). Yield = 0.143 g (86%), mp = 135–136 °C. ^{1}H NMR (700 MHz, Benzene-d_6) δ = 7.86 (d, J = 8.1 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 6.73 (d, J = 8.0 Hz, 2H), 4.23 (dd, J = 2.6, 1.5 Hz, 1H, Cp), 4.21 (dd, J = 2.6, 1.5 Hz, 1H, Cp), 4.02 (s, 5H, Cp), 3.96 (t, J = 2.6 Hz, 1H, Cp), 1.85 (s, 3H, CH_3). ^{13}C NMR (176 MHz, Benzene-d_6) δ = 142.4, 141.8, 141.0, 131.1, 129.8, 129.6, 129.4, 126.4, 125.9, 125.6 (q, J = 3 Hz), 124.9, 95.3 (Cp), 87.4 (Cp), 73.0 (Cp), 72.5 (Cp), 72.3 (Cp), 70.0 (Cp), 21.5 (CH_3). HR-MS (ESI): calcd. for $C_{24}H_{19}F_3FeOS$ ($[M+H]^+$): 469.0531, found: 469.0521.

Synthesis of 1-(4-trifluoromethylphenyl)-2-(*p*-tolylsulfinyl) ferrocene (**3e**) from 4-bromobenzotrifluoride: The quantities involved are as follows. Compound **2** (0.150 g, 0.27 mmol), 4-bromobenzotrifluoride (0.151 g, 0.67 mmol), sodium iodide (0.161 g, 1.07 mmol) and $Pd(PPh_3)_4$ (0.006 g, 2.0 mol %). After refluxing for 4 h the title compound was purified by flash column chromatography (*n*-hexane: EtOAc 4:1). Yield = 0.036 g (28%).

1-(3-Trifluoromethylphenyl)-2-(*p*-tolylsulfinyl)ferrocene (**3f**): The quantities involved are as follows. Compound **2** (0.200 g, 0.36 mmol), 3-iodobenzotrifluoride (0.240 g, 0.89 mmol), sodium iodide (0.240 g, 1.4 mmol) and $Pd(PPh_3)_4$ (0.012 g, 2.0 mol %). After refluxing for 12 h the title compound was purified by flash column chromatography (*n*-hexane: EtOAc 4:1). Yield = 0.125 g (75%), mp = 138–140 °C. ^{1}H NMR (700 MHz, Benzene-d_6) δ = 8.16 (s, 1H, ArH), 8.12 (d, J = 7.8 Hz, 1H, ArH), 7.47 (d, J = 7.2 Hz, 2H, ArH), 7.20 (d, J = 7.8 Hz, 1H, ArH), 6.95 (t, J = 7.8 Hz, 1H, ArH), 6.73 (d, J = 7.2 Hz, 2H, ArH), 4.26 (dd, J = 2.8, 1.6 Hz, 1H, Cp), 4.19 (dd, J = 2.8, 1.6 Hz, 1H, Cp), 4.05 (s, 5H, Cp), 3.95 (t, J = 2.8, 1H, Cp), 1.86 (s, 3H, CH_3). ^{13}C NMR (176 MHz, Benzene-d_6) δ = 142.0, 140.4, 138.3, 134.0, 130.7, 130.6, 130.4, 129.4, 127.5, 127.1 (q, J = 4 Hz), 126.0, 125.3, 123.9 (q, J = 3 Hz), 94.4 (Cp), 86.7 (Cp), 72.3 (Cp), 71.4 (Cp), 71.4 (Cp), 69.0 (Cp), 20.6 (CH_3). HR-MS (ESI): calcd. for $C_{24}H_{19}F_3FeOS$ ($[M+H]^+$): 469.0531, found: 469.0599.

1-(2-Trifluoromethylphenyl)-2-(*p*-tolylsulfinyl)ferrocene (**3g**): The quantities involved are as follows. Compound **2** (0.200 g, 0.36 mmol), 2-iodobenzotrifluoride (0.240 g, 0.89 mmol), sodium iodide (0.214 g, 1.4 mmol) and $Pd(PPh_3)_4$ (0.012 g, 2.0 mol %). After refluxing for 12 h the title compound was purified by flash column chromatography (*n*-hexane: EtOAc 4:1). Yield = 0.040 g (27%), mp = 135–136 °C. ^{1}H NMR (700 MHz, Benzene-d_6) δ = 8.70 (d, J = 7.8 Hz, 1H, ArH), 7.24 (t, J = 7.7 Hz, 1H, ArH), 7.20 (d, J = 7.9 Hz, 1H, ArH), 7.10 (d, J = 7.9 Hz, 2H, ArH), 6.88 (t, J = 7.7 Hz, 1H, ArH), 6.66 (d, J = 7.9 Hz, 2H, ArH), 4.46 (dd, J = 2.6 Hz, 1H, Cp), 4.37 (dd, J = 2.6 Hz, 1.5 Hz, 1H, Cp), 4.26 (s, 5H, Cp), 3.96 (t, J = 2.6 Hz, 1H, Cp), 1.89 (s, 3H, CH_3). ^{13}C NMR (176 MHz, Benzene-d_6) δ = 141.7, 139.7, 138.3, 134.1, 130.6, 130.1, 128.9, 127.7, 125.0 (q, J = 6 Hz), 124.3, 123.9, 96.8 (Cp), 87.9 (Cp), 73.1 (Cp), 71.8 (Cp), 71.6 (Cp), 68.3 (Cp), 21.0 (CH_3). HR-MS (ESI): calcd. for $C_{24}H_{19}F_3FeOS$ ($[M+H]^+$): 469.0531, found: 469.0477.

1-(4-Nitrophenyl)-2-(*p*-tolylsulfinyl)ferrocene (**3h**): The quantities involved are as follows. Compound **2** (0.280 g, 0.5 mmol), 1-iodo-4-nitrobenzene (0.310 g, 1.25 mmol), sodium iodide (0.300 g, 2.0 mmol) and $Pd(PPh_3)_4$ (0.012 g, 2.0 mol%). After refluxing for 4 h the title compound was purified by flash column chromatography (*n*-hexane: EtOAc 3:1). Yield = 0.17 g (76%), mp = 205–206 °C. ^{1}H NMR (700 MHz, Benzene-d_6) δ = 7.84 (d, J = 8.7 Hz, 2H, ArH), 7.74 (d, J = 8.7 Hz, 2H, ArH), 7.46 (d, J = 7.9 Hz, 2H, ArH), 6.72 (d, J = 7.9 Hz, 2H, ArH), 4.26 (s, 1H, Cp), 4.18 (s, 1H, Cp), 4.02 (s, 5H, Cp), 3.97 (s, 1H, Cp), 1.83 (s, 3H, CH_3). ^{13}C NMR (176 MHz, Benzene-d_6) δ = 146.5, 144.2, 141.4, 140.3, 130.1, 129.1, 127.9, 124.9, 122.9, 95.0 (Cp), 85.0 (Cp), 73.2 (Cp), 71.7 (Cp), 71.5 (Cp), 69.5 (Cp), 20.6 (CH_3). HR-MS (ESI): calcd. for $C_{23}H_{19}FeNO_3S$ ($[M+H]^+$): 446.0508, found: 446.0518.

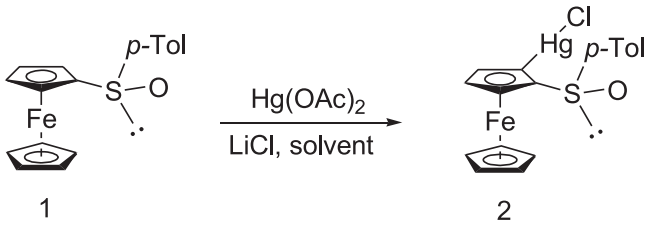
1-(Tolyl)-2-(*p*-tolylsulfinyl)ferrocene (**3i**): The quantities involved are as follows. Compound **2** (0.400 g, 0.72 mmol), 1-iodo-4-methyl benzene (0.389 g, 1.78 mmol), sodium iodide (1.067 g, 2.86 mmol) and $Pd(PPh_3)_4$ (0.016 g, 2.0 mol%). After refluxing for 4 h the title compound was purified by flash column chromatography (*n*-hexane: EtOAc 3:1). Yield = 0.052 g (17%), mp = 120–130 °C. ^{1}H NMR (700 MHz, Benzene-d_6) δ = 7.95 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 7.8 Hz, 2H), 7.03 (d, J = 7.8 Hz, 2H), 6.81 (d, J = 8.0 Hz, 2H), 4.41 (d, J = 2.0 Hz, 1H), 4.11 (t, J = 2.1 Hz, 1H), 4.02 (s, 5H), 3.97 (t, J = 2.6 Hz, 1H), 2.10 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (176 MHz, Benzene-d_6) δ = 142.0, 140.3, 136.7, 133.6, 130.2, 129.2, 128.9, 125.7, 93.6 (Cp), 89.7 (Cp), 72.0 (Cp), 71.4 (Cp), 70.8 (Cp), 69.0 (Cp), 21.0 (CH_3), 20.9 (CH_3). HR-MS (ESI): calcd. for $C_{24}H_{22}FeOS$ ($[M+Na]^+$): 437.0557, found: 437.0633.

Control Experiment (Synthesis of compound **5**): In a Schlenk tube, 0.280 g (0.50 mmol) of compound **2** and 0.300 g (2.0 mmol) of NaI were placed. Subsequently 3 mL of dry THF and 2 mL of dry acetone were added and the reaction mixture was refluxed for 12 h. The reaction mixture was filtered through a pad of silica, washed with 2 × 20 mL of THF and the resultant filtrate was concentrated. The crude product was purified by flash column chromatography using *n*-hexane and ethyl acetate as an eluent to afford the desired product in 85% yield (0.23 g). mp. >230 °C (decomposes). ^{1}H NMR (400 MHz, Benzene-d_6): δ = 7.58 (d, J = 8 Hz, 2H, ArH), 6.84 (d, J = 8 Hz, 2H, ArH), 4.77 (s, 5H), 4.60 (s, 1H), 4.39 (s, 1H), 4.29 (s, 1H), 4.05 (ferrocene impurity), 1.90 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, Benzene-d_6): δ = 146.2, 140.1, 129.7, 124.2, 102.7 (Cp), 95.4 (Cp), 77.5 (Cp), 72.6 (Cp), 70.6 (Cp), 69.7 (Cp), 21.0 (CH_3) ppm. HR-MS (ESI): calcd. for $C_{34}H_{30}Fe_2HgO_2S_2$ ($[M+H]^+$): 849.0169, found: 849.0157.

3. Results and discussion

3.1. Synthesis and characterization of compound 2

Ortho-mercuration of substituted ferrocenes [25], attract a great deal of interest owing to the fact that they can be used a) to synthesis other organometallic compounds through trasmetallation and b) as reagents in organic synthesis. Although, synthesis of *ortho*-mercury ferrocene using different functionalities like azobenzenes, benzylideneanilines, phenylhydrazenes *etc*. have been reported [25]; however, to the best of our knowledge, there are no reports on the *ortho*-mercuration of ferrocenyl *p*-tolyl sulfoxide. The starting compound ferrocenyl *p*-tolyl sulfoxide (**1**) has been synthesized using the well-established Kagan and co-workers methodology [15]. O*rtho*-mercuration of the sulfinyl ferrocene proceeded smoothly to produce 2-chloromercurated ferrocenylsulfoxide (**2**) in moderate yield (Scheme 1). The ^{1}H NMR of compound **2** shows three signals of equal intensity for the



Scheme 1. Synthesis of 1-(*p*-tolylsulfinyl)-2-(chloromercurio)ferrocene (**2**).

substituted Cp ring ($\delta = 4.33$, 3.96, & 3.62 ppm) and one signal for the unsubstituted Cp ring at $\delta = 4.05$ ppm, which is consistent with 1,2-disubstituted ferrocenes. Single crystal X-ray diffraction analysis was carried out to confirm the formation of compound **2**. As shown in Fig. 1, the oxygen (O) atom points towards the mercury (Hg) atom. The distance between O and Hg atom (2.875 (5) Å) is shorter than the sum of the van der Waals radii (for Hg 1.73–2.00 Å [26]; for O 1.54 Å [27]), thus indicating an interaction between the oxygen and the mercury atom. Such type of weak interactions have been reported in the literature [19,28–30]. We believe that this oxygen-mercury interaction is responsible for the *ortho*-mercuration of compound **1** into compound **2**.

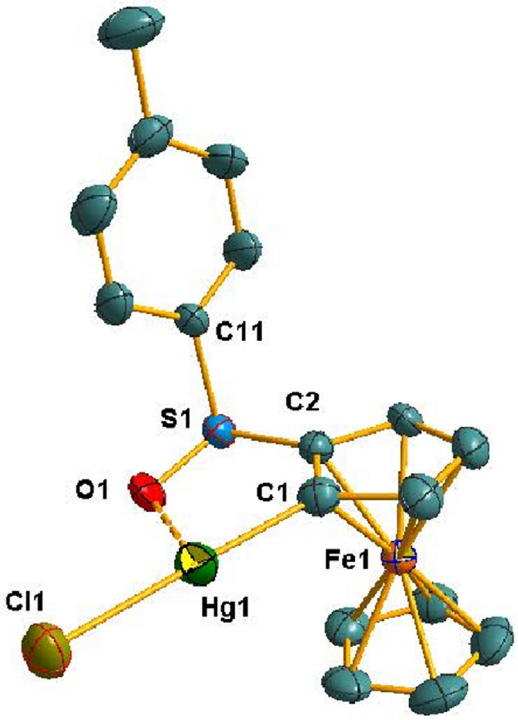


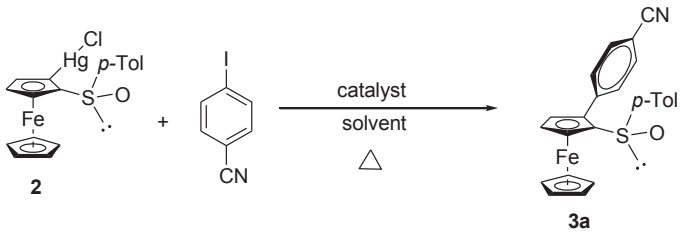
Fig. 1. Molecular structure of compound **2** (ORTEP, 50% probability). Hydrogen atoms are removed for clarity. Selected bond lengths (Å) and bond angles (°): Hg1-C1 2.035(5), Hg1-Cl1 2.308(1), S1-O1 1.489(3), C1-Hg1-Cl1 178.9(1).

3.2. Reaction of compound 2 to form compound 3

Inspired by Beletskaya and co-workers [31] work, we tested cross-coupling of 1-(*p*-tolylsulfinyl)-2-(chloromercurio)ferrocene (**2**) with 4-iodobenzonitrile as the model substrate. We first studied the reaction using 1.5 equivalents of CuO as an oxidant in the presence of 5 mol % $PdCl_2$(dppf) in anhydrous dimethylformamide (DMF) at 100 °C under argon atmosphere but failed to get the desired product (Table 1, entry 1). Various palladium based catalysts, solvents, additives were screened and found that the reaction proceeded smoothly with 2 mol % of $Pd(PPh_3)_4$ (Table 1, entry 6) in mixture of solvents (THF/acetone) at reflux condition. To our delight, the desired product was isolated in 90% yield. Under the above optimized reaction conditions, the scope of substrates were investigated. As shown in Table 2, various substituted aryl iodides bearing electron withdrawing groups were converted to the corresponding products with good to moderate isolated yields. The reaction of 4-iodobromobenzene with compound **2** resulted in 1-(4-bromophenyl)-2-(*p*-tolylsulfinyl)ferrocene (**3d**) in high yield. *p*, *m*, *o*-Iodobenzotrifluorides were converted to the corresponding products (**3e**, **3f** & **3g**) with moderate yields. However, the *o*-iodobenzotrifluoride afforded only low yield (27%). Reaction of 1-iodo-4-methylbenzene resulted in the corresponding product **3i** in low yield (17%). Aryl bromides such as 4-bromobenzonitrile and 4-bromobenzotrifluoride got converted to their respective products in 48% and 28% yields respectively, however bromobenzene was not active enough to give the desired product under the experimental conditions. Moreover, aryl chlorides failed to afford the respective products under the optimized conditions.

All coupled products (**3a**-**3i**) were confirmed using ^1H, ^{13}C and HRMS. Product **3a**, was further confirmed using single crystal X-ray analysis (Fig. 2). The X-ray analysis revealed one molecule in the asymmetric unit. The Cp//Cp tilt angle is 0.89°. The angle between cyclopentadienyl (Cp) and the CN-phenyl group is 37.68°. The oxygen atom on sulfur (-SO-) points upwards and the tolyl points away from the CN-Phenyl (see Fig. 2).

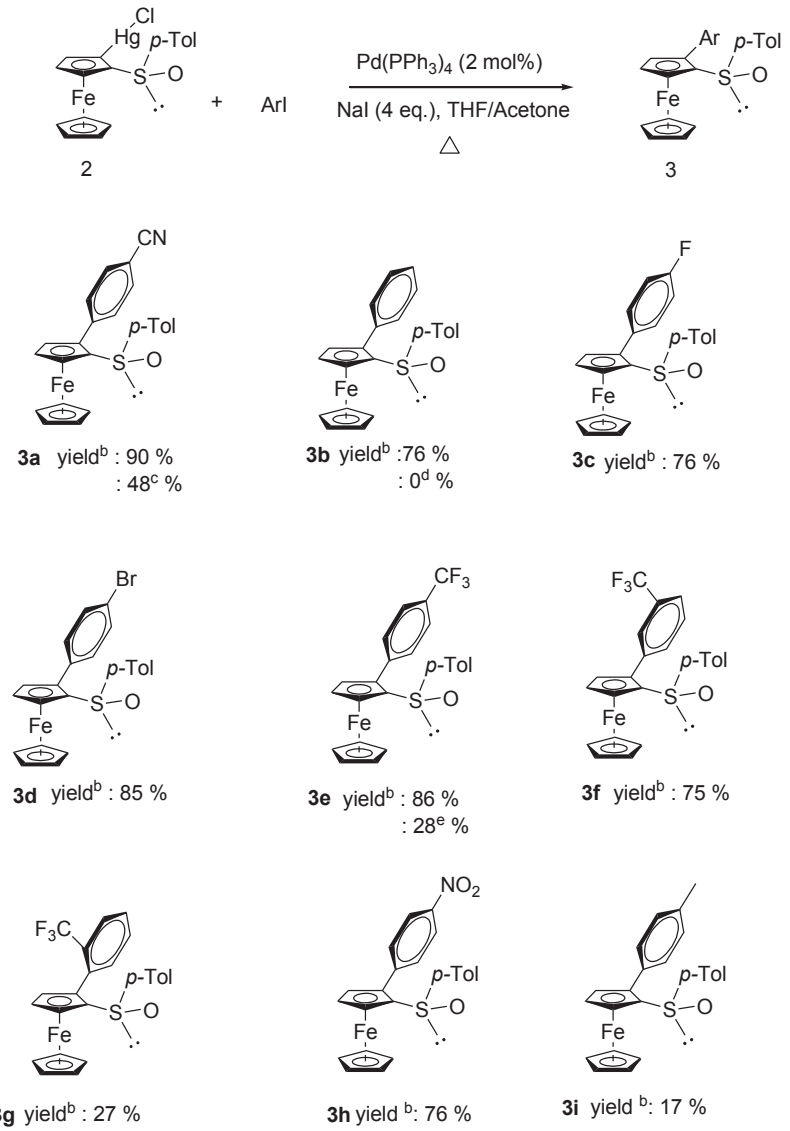
Table 1
Cross-coupling reaction between 4-iodobenzonitrile and compound **2**.[a]



S. No	Catalyst	Cat. Loading (mol %)	Additives (eq.)	Solvents[b]	Temp. (°C)	Yield (%)[c]
1	$PdCl_2$(dppf)	5	CuO (1.5)	DMF	100	–
2	$Pd(dba)_2$	5	$ZnCl_2$ (1.5)	THF	80	–
3	$Pd(PPh_3)_4$	5	K_2CO_3 (4)	THF	80	–
4	$Pd(PPh_3)_4$	5	NaI (4)	THF/Acetone	80	95
5	$Pd(PPh_3)_4$	5	–	THF/Acetone	80	–
6	$Pd(PPh_3)_4$	2	NaI (4)	THF/Acetone	80	90

[a] Reaction conditions: Compound **2** (0.50 mmol), 4-iodobenzonitrile (1.25 mmol).
[b] All reactions were carried out under inert atmosphere.
[c] Isolated yield.

Table 2
Cross-coupling reaction between different aryl halides and compound **2**.



[a]Reaction conditions: Compound **2** (0.10 mmol), aryl iodides (0.25 mmol), $Pd(PPh_3)_4$ (2 mol%), and NaI (0.40 mmol) in 1 mL dry acetone and 2 mL of dry THF at reflux condition.
[b]Isolated yield after flash column chromatography. [c]4-Bromobenzonitrile is used. [d]Bromobenzene is used. [e]4-Bromobenzotrifluoride is used.

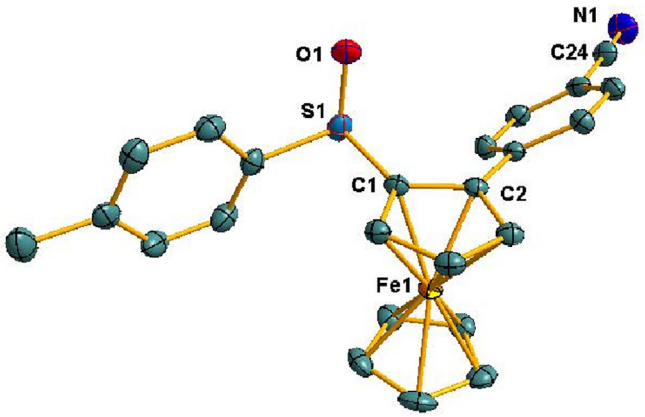


Fig. 2. Molecular structure of **3a** (ORTEP, 50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): C1-S1 1.776(3), S1-O1 1.494(2), C1-C2 1.449(3), C24-N1 1.139(4), C1-S1-O1 105.7(1), C1-S1-C11 106.9(1), C2-C1-S1 123.3(2), N1-C24-C21 177.2(3).

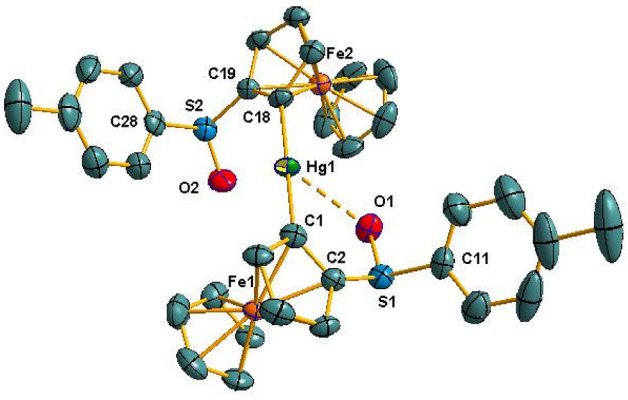
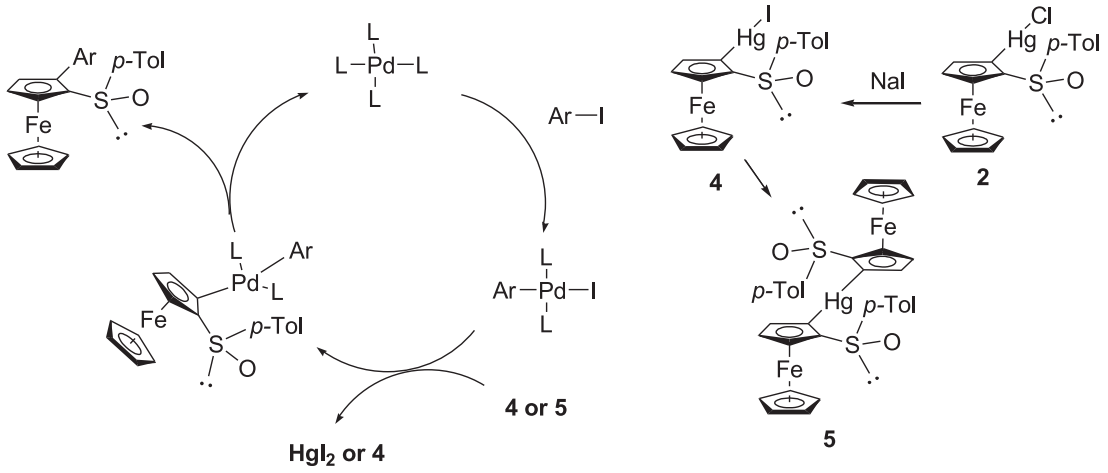


Fig. 3. Molecular structure of **5** (ORTEP, 50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Hg1-C1 2.051(6), Hg1-C18 2.056(6), S1-O1 1.493(5), S2-O2 1.478(5), C1-Hg1-C18 173.7(2), $Cp_{centroid}$-Hg-C1 176.5, $Cp_{centroid}$-Hg-C18 177.7.



Scheme 2. Proposed mechanism for the palladium-catalyzed cross-coupling of compound 2 with aryl halides.

3.3. Proposed mechanism

We propose a plausible mechanism based on LC/MS, X-ray analysis and based on the previous literature [31]. As shown in Scheme 2, the mechanism for the cross-coupling of aryl halide and compound **2** is analogous to other organometallic coupling reactions. To examine the species involved during transformation, we recorded the ESI of the reaction mixture of one of the reactions and found fragment ion of m/z = 651.9037 and m/z = 848.0237 which corresponds to compound **4** and **5** respectively (supporting information).

We have found the formation of symmetrized (Fc-SO-tolyl))$_2$Hg (**5**) as a side product under our optimized reaction conditions without the use of aryl iodide and palladium catalyst. It has been reported in literature [32] that treatment of chloromercury organic compounds in the presence of sodium iodide results in symmetrization or dimerization or cyclization depending on the starting materials. To know the role of compound **5**, a control experiment was carried out using compound **5** as the substrate and 4-fluorophenyl iodide as the arylating agent. We found a higher yield of product 3c under similar conditions discussed *vide supra*. We are lucky enough to have the crystal structure of **5** also. As shown in Fig. 3, two (tolyl sulfoxide) ferrocenyl moieties are linked through a mercury atom. The Hg1-C1 (2.051 (6) Å) and Hg1-C18 (2.056(6) Å) bond lengths are comparable to those found in related organomercury compounds [19,29,30]. The molecular structure of compound **5** also shows the coordination to one of the oxygen atoms with mercury atom. The Hg1···O1 (2.824(4) Å) bond length is shorter than the sum of the van der Waals radii of Hg and O, where as the Hg1···C18 bond length (3.374(6) Å) shows a very weak interaction between O and Hg. The $Cp_{centroid}$-Hg-C angles of 176.5° and 177.7° indicates almost linear coordination geometry at Hg, however C1-Hg2-C18 angle of 173.6° reveals a slight tilting toward O1 atom associated with binding of the −SO ligand.

4. Conclusions

In summary, we have developed a new methodology for the synthesis of 1,2-disubstituted ferrocenes from ferrocenyl *p*-tolyl sulfoxide. This protocol furnished moderate to good yield. We have also showed that sulfoxide moiety (FcSO) acts as a versatile functional group to direct mercury to form 1-(*p*-tolylsulfinyl)-2-(chloromercurio)ferrocene (**2**) as an isolable air and moisture stable compound. Further studies to make planar chiral 1,2-disubstituted ferrocenes are in progress.

Acknowledgements

KV thanks the Department of Science and Technology (DST), New Delhi (SR/S2/RJN-49/2011 and SR/S1/IC-58/2012) and NISER for financial support. RVRNC, RM, VM, KD thank CSIR, New Delhi for research fellowship.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jorganchem.2017.10.028.

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