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# Synthesis and some reactions of ferrocenylacetylenes

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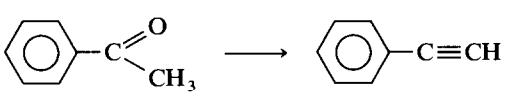
**Abstract**

The conversion of acetylferrocene or diacetylferrocene into ethynylferrocene **1** or diethynylferrocene **4**, respectively, is achieved in good yield in a one-pot synthesis using Negishi's reagent. The diethynylferrocene is isolated as its trimethylsilyl derivative **5**. The complexes **1** and **5** undergo various nucleophilic substitution reactions, resulting in new ferrocenyl derivatives.

## Introduction

Ferrocene derivatives are starting material for the synthesis of more complicated organometallic compounds. The most recent report of improved synthesis of ferrocenyl acetylenes dates back to 1966 [1]. This method consists of treating acetylferrocene with an excess of phosphorus oxychloride and dimethylformamide to give the chloroaldehyde FcCCl=CHCHO (Fc = ferrocenyl or, as appropriate, ferrocenechyl) in 87% yield. This was further transformed into ethynylferrocene **1** in 88% yield, by heating it in a basic aqueous dioxan solution. A few ferrocene acetylenes were prepared using slight modifications of this method [2,3]. However, attempts to synthesise diethynylferrocene **4** from diacetylferrocene using the above method were unsuccessful. Instead a more indirect method was employed to obtain the diethynyl ferrocenyl derivatives, involving coupling of 1,1'-diodoferrocene [4] with cuprous phenylacetylide. These ferrocenyl acetylenes are useful starting materials for the synthesis of other acetylenic derivatives [5].

Here we report a direct approach to synthesise ferrocenylacetylenes using Negishi's method [6] (eq. 1) for the conversion of a ketone group into an acetylenic group in a one-pot synthesis.

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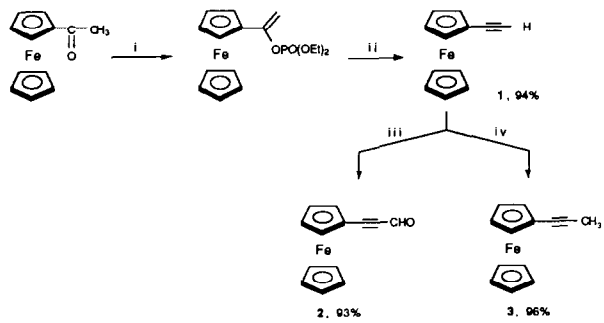



Scheme 1. i: 1.05 equiv. LDA, 1.1 equiv. $ClPO(OEt)_2$. ii: 2.2 equiv. LDA, $H_2O$. iii: 1.05 equiv. $Li^nBu$, DMF. iv: 1.05 equiv. $Li^nBu$, MeI.

## Results and discussion

Both acetylferrocene and diacetylferrocene are commercially available starting materials, and can be obtained quantitatively by the Friedel–Crafts acylation of ferrocene [7]. Acetylferrocene, upon treatment with lithium diisopropylamide (LDA) followed by diethylchlorophosphate, then 2.5 equiv. of LDA and hydrolysis gives ethynylferrocene **1** in 94% overall yield.

Compound **1** undergoes nucleophilic substitution reactions. Formation of acetylide ion upon treatment with $Li^nBu$ followed by addition of dimethylformamide (DMF) or MeI results in complexes **2** (93%) or **3** (96%), respectively (Scheme 1). The carboxaldehyde **2** is a potential precursor for the synthesis of various ferrocene derivatives.

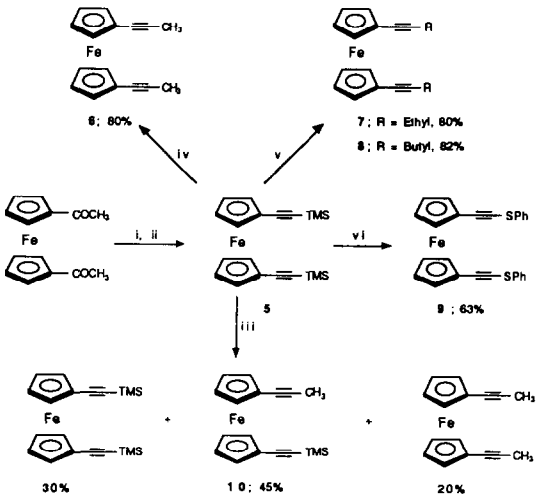
Similarly, treatment of diacetylferrocene using Negishi's method gives an unstable diethynyl complex which can be converted to a stable trimethylsilane derivative **5**. The complex **5** undergoes electrophilic substitution reactions to give stable crystalline solids in good yield.

These reactions are shown in Scheme 2. Bis(trimethylsilyl)butadiyne can undergo selective cleavage of only one of the silylacetylene bonds, to give lithium(trimethylsilyl)butadiynyl [8]. We attempted a similar selective functionalisation of compound **5** by treatment with 1 equiv. of LiMe (LiBr) followed by addition of MeI. Instead of the expected product **10**, a mixture of complexes **10** and **6** and unreacted starting material was obtained. Hexamethylphosphorus triamide (HMPT) was necessary as a co-solvent for all nucleophilic substitution reactions except with iodomethane, which reacts cleanly in THF.

Attempts to obtain a dicarboxaldehyde, homologous with **2**, were unsuccessful.

## Conclusion

A facile, convenient method for the preparation of monoethynyl and diethynyl derivatives of ferrocene is outlined in this paper. The diethynylferrocene is unstable, but can be converted to its trimethylsilyl derivative. A new lithium reagent is obtained upon treatment of this ferrocenyl diacetylene with LiMe (LiBr) which undergoes various nucleophilic substitution reactions. This method provides a straightforward synthesis to ferrocenes containing new ligands.




Scheme 2. i: 2.2 equiv. $ClPO(OEt)_2$. ii: 4.4 equiv. LDA, $Me_3SiCl$ (TMCl). iii: 1 equiv. LiMe (LiBr), MeI. iv: 3 equiv. LiMe (LiBr), MeI. v: 3 equiv. LiMe (LiBr), RI in HMPT. vi: 3 equiv. LiMe (LiBr), PhSSPh in HMPT.

## Experimental section

All manipulations were done under an inert atmosphere. Elemental analyses were performed by the microanalysis service of the CNRS at Gif-sur-Yvette. Acetyl- and diacetyl-ferrocene were purchased from Aldrich. Solvents were purified prior to use. Lithium diisopropylamide (LDA) was freshly prepared by addition of $Li^nBu$ to a solution of diisopropylamine in THF. The $^1H$ NMR data are given in Table 1.

Table 1

$^1H$ NMR data for ferrocenyl derivatives. Spectra were recorded on Brüker 200 or 250 MHz spectrometer.

| Compound | No. | Proton chemical shift assignments, $\delta$ | | |
|---|---|---|---|---|
| | | $C_5H_5$ | $C_5H_4$ | Others |
| Fc−C≡C−H | 1 | 4.2 | 4.18–4.45 | 2.7 (1H) |
| Fc−C≡C−$CH_3$ | 2 | 4.2 | 4.35 (t), 4.25 (t) $J = 16$ Hz | 1.95 (3H) |
| Fc−C≡C−CHO | 3 | 4.3 | 4.45; 4.65 | 9.3 (1H) |
| Fc−(C≡C−TMS)$_2$ | 5 | – | 4.4; 4.2 | 0.25 (18H) |
| Fc−(C≡C−$CH_3$)$_2$ | 6 | – | 4.35; 4.15 | 1.98 (6H) |
| Fc−(C≡C−$C_2H_5$)$_2$ | 7 | – | 4.35; 4.15 | 1.2:t, 6H $J = 6$ Hz<br>2.3:q, 4H $J = 6$ Hz |
| Fc−(C≡C−Bu)$_2$ | 8 | – | 4.35; 4.15 | 0.9:t, 4H $J = 6$ Hz<br>1.5:m, 8H<br>2.3:t, 6H $J = 6$ Hz |
| Fc−(C≡C−SPh)$_2$ | 9 | – | 4.55; 4.35 | 7.2–7.55<br>(m, 10H) |

*Ethynylferrocene 1.* To a solution of 14 g (61 mmol) of acetylferrocene in THF (50 ml) at −78°C were added dropwise 1.1 equiv. of LDA in THF. After 1 h at −78°C, 1.05 equiv. (9.3 ml, 64 mmol) of diethylchlorophosphate were added, and the temperature was maintained at −78°C during an additional 1 h, after which the reaction mixture was raised to room temperature. An additional 2.3 equiv. (140 mmol) of LDA solution in THF were added at −78°C. The solution was brought to room temperature and then hydrolysed at 0°C. The organic layer was extracted with $CH_2Cl_2$ and dried over $MgSO_4$. The yellow oil obtained after evaporation of the solvent was purified by flash chromatography using a 2:1 pentane–ether mixture.. The first fraction gave yellow oil which was crystallised at 0°C from pentane (12.1 g: 94%). Anal. Found: C, 68.51; H, 4.82. $C_{12}H_{10}Fe$ calc.: C, 68.61; H, 4.80.

*Ferrocenyl(formyl)acetylene 2.* A solution of Li$^n$Bu (3.2 ml, 1.6 *M*, 1.05 equiv., 5 mmol) in hexane was added to 1 g (4.8 mmol) of ethynylferrocene in THF at −78°C. After 30 min, an excess of DMF (1 ml, 13 mmol) was added. After 1 h at −78°C, the solution was brought to room temperature and poured over 50 ml of an ice–water mixture containing 5 ml of conc. HCl. A violet coloration was observed. The solution was neutralised with $NaHCO_3$, and the red solution so formed was extracted with ether, dried and 1.05 g (4.4 mmol, 93%) of red crystalline solid was obtained upon removal of solvent. Anal. Found: C, 65.74; H, 4.43. $C_{13}H_{10}OFe$ calc.: C, 65.59; H, 4.23.

*Ferrocenylpropyne 3.* A solution of Li$^n$Bu (1.30 ml, 1.6 *M*, 1.1 equiv., 2 mmol) in hexane was added to 0.4 g (1.9 mmol) of ethynylferrocene in 30 ml of THF at −78°C. After 30 min, an excess of MeI (0.5 ml, 8 mmol) was added. The solution was brought to room temperature and stirred for 1 h, and then hydrolysed at 0°C. Extraction with $CH_2Cl_2$, washing with water and removal of solvent gave 410 mg (1.8 mmol, 96%) of brown solid. Anal. Found: C, 69.96; H, 5.68. $C_{13}H_{12}Fe$ calc.: C, 69.68; H, 5.39.

*1,1'-Bis(trimethylsilylethynyl)ferrocene 5.* Complex **5** was prepared by a similar method to that used for complex **1**. Just before the hydrolysis step, an excess of (10 equiv.) trimethylsilyl chloride was added at −78°C. The reaction mixture was brought to room temperature. Hydrolysis at 0°C was followed by extraction with ether. The ether extract was dried over $MgSO_4$ and the ether was evaporated. Flash chromatography in pentane gave a brownish yellow solid in 63% yield. Anal. Found: C, 63.04; H, 6.88. $C_{20}H_{26}FeSi_2$ calc.: C, 63.48; H, 6.92.

*1,1'-Bis(methylethynyl)ferrocene 6.* To a THF solution (30 ml) of 0.4 g (1.05 mol) of **5** at −78°C, 1.6 ml (3 equiv.) of 2 *M* LiMe (LiBr) in ether solution was added. The solution was left stirring overnight at room temperature. An excess of freshly distilled MeI was added at −78°C. After 1 h at room temperature, the solution was hydrolysed, extracted with $CH_2Cl_2$, and dried. Removal of the solvent gave an orange solid which was recrystallised from pentane (220 mg, 0.84 mmol, 80%). Anal. Found: C, 72.95; H, 5.32. $C_{16}H_{14}Fe$ calc.: C, 73.31; H, 5.38.

*1,1'-Bis(ethylethynyl)ferrocene 7.* The anion was prepared analogous to **6** using 0.4 g (1.05 mmol) of **5** and 1.6 ml (3 equiv.) of 2 *M* LiMe (LiBr). Ethyliodide (0.5 ml) in HMPT (10 ml) was added at −78°C. The HMPT was removed by successive washings with water. A yellow oil was obtained after the usual work-up. It was purified by filtering over $Al_2O_3$ in pentane (245 mg, 84 mmol, 80%). Anal. Found: C, 74.25; H, 6.44. $C_{18}H_{18}Fe$ calc.: C, 74.50; H, 6.25.

*1,1'-Bis(butylethynyl)ferrocene 8.* Complex **8** was prepared analogously to complex **7**, using butyl iodide, and was obtained in 82% yield. Anal. Found: C, 76.34; H, 7.52. $C_{22}H_{26}Fe$ calc.: C, 76.30; H, 7.56.

*1,1'-Bis(phenylthioethynyl)ferrocene 9.* The anion was prepared as above, using 0.4 g (1.05 mmol) of **5** and 1.6 ml (3 equiv.) of 2 *M* LiMe (LiBr) solution in ether. Diphenyl disulphide (0.8 g, 3.7 mmol) in HMPT (10 ml) was added. The usual work-up gave a red oil. The first band eluted with flash chromatography using pentane gave red crystals (300 mg, 0.66 mmol, 63%). Anal. Found : C, 69.41; H, 4.29; S, 13.99. $C_{26}H_{18}S_2Fe$ calc.: C, 69.33; H, 4.29; S, 14.24.

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