SYNTHESIS OF DIFERROCENYLETHYNE BY MOLYBDENUM-CATALYZED METATHESIS OF 1-FERROCENYLPROP-1-YNE

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Diferrocenylethyne (**1**) was synthesized by metathesis of 1-ferrocenylprop-1-yne using various catalytic systems based on $[Mo(CO)_6]$ (5 mole %) and a chlorophenol (30 mole %) in toluene. The yields varied for different chlorophenols; the best conversions were obtained with 2,5-dichlorophenol (66%) and 4-chlorophenol (55%). Alkyne **1** was further reduced to the known (*E*)-1,2-diferrocenylethene and 1,2-diferrocenylethane, and its solid-state structure determined by single-crystal X-ray diffraction.
**Keywords**: Metallocenes; Ferrocene; Alkynes; Metathesis; Diferrocenylethyne; Reductions; X-Ray crystallography.

Metathesis of internal alkynes represents a convenient method for the preparation of symmetrically substituted alkynes, avoiding sometimes cumbersome sequential double alkylation of ethyne or the use of intermediates that are difficult to synthesize. The preparation of diferrocenylethyne, $FcC≡CFc$ (**1**; Fc = ferrocenyl) can be regarded a representative example as this alkyne has been obtained by cross-coupling of ferrocenylethyne with iodoferrocene[1] or from pyrolysis of phosphorane $FcC(O)C(Fc)=PPh_3$ (ref.[2]). While the preparation of ferrocenylethyne possesses no difficulties and several simple and high yielding procedures have been reported in the literature[1a,3], the synthesis of iodoferrocene is rather tedious, requiring manipulation with hazardous materials (such as organomercury, -thallium and -tin compounds) and separation of mono- and 1,1′-disubstituted ferrocenes[4]. From this point of view, a method affording **1** from a better accessible starting material is desirable. In this contribution, we report about an alternative approach to **1** by molybdenum-catalyzed metathesis of 1-ferrocenylprop-1-yne (**2**), and further about catalytic hydrogenation of **1** to

(*E*)-1,2-diferrocenylethene (**3**) and 1,2-diferrocenylethane (**4**), and the crystal structure of **1**.

RESULTS AND DISCUSSION

Alkyne metathesis can be conveniently accomplished using a structurally unknown catalyst formed in situ from $[Mo(CO)_6]$ and 4-chlorophenol in refluxing chlorobenzene or toluene[5]. This catalytic system has been successfully applied for the preparation of various diarylethynes[6]. Considering these results, we reasoned that this method could be also applied for the preparation of **1** from alkynylferrocenes. Thus, the metathesis reaction was performed with 1-ferrocenylprop-1-yne (**2**; 1 mmol), $[Mo(CO)_6]$ (5 mole %), and chlorophenol (30 mole %) in toluene (3 ml) at 120 °C for 12 h (Scheme 1).

$$FcC\equiv CMe \xrightarrow{[Mo]} FcC\equiv CFc + MeC\equiv CMe$$
$$\mathbf{2} \qquad\qquad\qquad \mathbf{1}$$

SCHEME 1
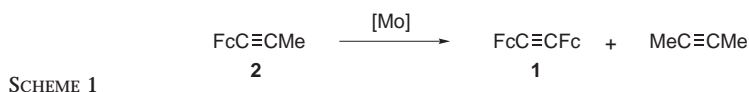
The reaction was carried out with various chlorophenols to assess their effect on the course of the reaction; the results are summarized in Table I. The best yields of **1** were obtained with 4-chlorophenol and 2,5-dichlorophenol (55 and 66%, respectively); the other, more chlorine-substituted phenols gave rather low yields. This indicates that some steric hindrance at the hydroxyl group is beneficial for the course of the reaction, phenols substituted with halogen in *ortho* position giving better yields that the respective *para* isomers. However, a large steric hindrance (*e.g.*, by substitution at both *ortho* positions) hinders the reaction. This observation is supported by a recent report on the application of various chloro- and fluorophenols in similar metathesis reactions[7]. Besides, the acidity of the halophenol (*i.e.*, an electronic influence) may also play an important role.

TABLE I
Effect of chlorophenol on the ^{1}H NMR yield of **1**

Chlorophenol	Yield, %
4-Chlorophenol	55
2,5-Dihlorophenol	66
2,4,6-Trichlorophenol	13
2,3,4,5,6-Pentachlorophenol	8

As far as by-products are concerned, no other ferrocene compounds were identified in the reaction mixture apart from **1** and some unreacted **2**, though formation of some intractable, dark tarry materials was observed (no attempt was made to detect volatile but-2-yne as the expected side product). Some problems were encountered during the isolation of **1** since column chromatography on silica gel or alumina was not very efficient because of similar retention characteristics of the starting material and the product. Fortunately, a low solubility of **1** in common organic solvents at room temperature enabled its separation from other, more soluble reaction components by repeated crystalization from hot toluene. In such a way it was possible to obtain analytically pure **1** reproducibly in 40% isolated yields at 1 mmol scale and similar results were obtained when the reaction was scaled up four times.

Alkyne **1** was further subjected to catalytic hydrogenation in the presence of $Pd/CaCO_3$ and $Pd/CaCO_3$/quinoline catalytic systems in dichloromethane. While the former catalyst afforded the expected product of a complete triple-bond reduction, 1,2-diferrocenylethane (**4**; 96% yield at 50 μmol scale), hydrogenation with Lindlar catalyts[8] gave a mixture of **4** and (*E*)-1,2-diferrocenylethene (**3**; 65% isolated yield at 90 μmol scale) (Scheme 2). This apparently contrasts with the previous report that the reduction of **1** catalyzed with Lindlar catalyst gives pure (*Z*)-alkene in a near-to-quantitative yield. However, as this alkene easily isomerized to (*E*)-isomer in the presence of *p*-toluenesulfonic acid[2], it is likely that the kinetic product, the (*Z*)-alkene, is immediately isomerized by traces of HCl notoriously present in dichloromethane to afford the more stable (*E*)-isomer.

FcC≡CFc $\xrightarrow{\text{H}_2, \text{ Pd/CaCO}_3, \text{ quinoline}}$ FcCH₂CH₂Fc + (structure of **3**)

1   **4**
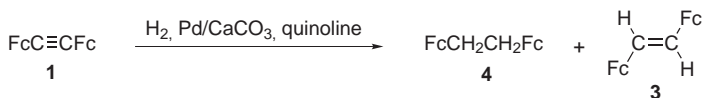
SCHEME 2

The Solid-State Structure of **1**

The molecular structure of alkyne **1** is shown in Fig. 1. The compound crystallizes with the symmetry of the monoclinic space group $P2_1/c$ with only the half of the molecule crystallographically independent ($Z = 2$) because the molecule is located so that the midpoint of the triple bond coincides with the crystallographic inversion centre. Due to the imposed symmetry, the molecule consists of two identical {FcC≡} parts and possesses exactly parallel, up-down oriented ferrocene moieties, which show only a negligible ring tilt (the dihedral angle of the least-squares cyclopentadienyl planes

is 1.8(3)°). The triple-bond length, $C(11)–C(11)^i$ 1.222(7) Å [i: $–x$, 1 – y, 1 – z], is slightly longer than those in, *e.g.*, $FcC≡CSiMe_3$ (1.189(7) Å (ref.[9])), $FcC≡C(C_6H_3Br_2-3,5)$ (1.16(1) Å) and $1,3,5-(FcC≡C)C_6H_3$ (1.15(1), 1.18(1) and 1.19(1) Å (ref.[10])), in 2,7-bis(ferrocenylethynyl)fluorene (1.20(1), 1.179(9) Å) and 2,7-bis(ferrocenylethynyl)fluoren-9-one (1.126(4), 1.133(4) Å (ref.[11])), and in $FcC≡C(C_6H_4CN-4)$ (1.190(5) Å (ref.[12])). The other metric parameters are quite unexceptional.

EXPERIMENTAL

Chemicals and Methods

All syntheses were carried under argon. Toluene was freshly distilled from sodium–benzophenone ketyl. 1-Ferrocenylprop-1-yne was prepared by metalation of ethynylferrocene with butyl lithium to $FcC≡CLi$, followed by an alkylation with MeI (ref.[13]). All other chemicals and solvents were used as received from commercial suppliers.
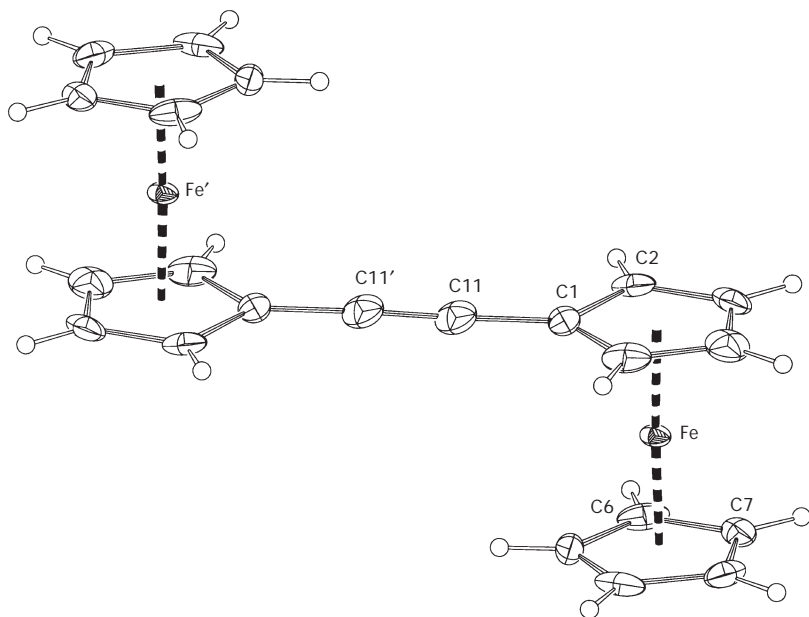

FIG. 1

A view of the molecular structure of **1** drawn at the 30% probability level. The selected distances (in Å) and angles (in °): Fe–Cg(1) 1.647(2), Fe–Cg(2) 1.654(2), Fe–C(Cp) 2.029(4)–2.052(5), C(1)–C(11) 1.420(7), $C(11)–C(11)^i$ 1.222(7), C–C(Cp) 1.372(7)–1.472(6); $C(1)–C(11)–C(11)^i$ 177.2(5). Cg(1) and Cg(2) are the centroids of the C(1–5) and C(6–10) cyclopentadienyl rings, respectively. The prime-labelled atoms are generated by the ($–x$, 1 – y, 1 – z) symmetry operation

NMR spectra were recorded on a Varian UNITY Inova 400 spectrometer (^{1}H, 399.95 MHz; ^{13}C, 100.58 MHz) at 298 K. Chemical shifts (δ, ppm) are given relative to internal tetramethylsilane. GC analyses were performed on a Shimadzu GC-17A chromatograph equipped with a ZB-5 column (5% phenyl, 95% dimethylpolysiloxane). Melting points were determined on a Kofler block and are uncorrected.

A Typical Procedure for the Preparation of 1

A solution of **2** (224 mg, 1.0 mmol), [Mo(CO)$_6$] (13 mg, 50 µmol), 4-chlorophenol (39 mg, 30 µl, 0.30 mmol) in toluene (3 ml) was heated to 120 °C for 12 h. The reaction mixture was diluted by toluene (20 ml), washed with 1 M aqueous NaOH (removal of chlorophenol), and dried over MgSO$_4$. Then, it was filtered over a short alumina column to remove some tarry material and precipitated molybdenum metal. The eluate was concentrated under vacuum and dissolved in minimum amount of boiling toluene. After standing overnight, the separated dark red crystals of **1** (they start to appear already upon cooling) were filtered off and the mother liquor evaporated and crystallized once again to recover a second crop of the product. In such a way, totally 158 mg (40%) of the alkyne **1** was obtained. ^{1}H NMR (CDCl$_3$): 4.20 (apparent t, 2 H, C$_5$H$_4$); 4.23 (s, 5 H, C$_5$H$_5$); 4.45 (apparent t, 2 H, C$_5$H$_4$). ^{13}C NMR: 66.32, 68.50, 69.98, 71.20, 83.93. M.p. 246–246.5 (dec.) °C (ref.[1b] gives 244–245 °C, ref.[2] 244–246 °C). HR MS calculated for C$_{22}$H$_{18}$Fe$_2$ (M$^{\bullet +}$) 394.0107, found 394.0093.

Preparation of (*E*)-1,2-Diferrocenylethene (3)

Pd/CaCO$_3$ (5 mole %) was placed into a flask and the flask was flushed several times with H$_2$. Then, a solution of **1** (35 mg, 0.09 mmol) and one small drop of quinoline in dichloromethane (2.5 ml) was introduced and the reaction mixture was stirred under hydrogen (ambient pressure) and monitored by GC chromatography. After *ca* 4 h, the mixture was filtered to remove the catalyst and the solvent evaporated under vacuum. The products of complete (**4**) and partial (**3**) hydrogenation were separated by fractional crystallization from hot toluene. A subsequent flash chromatografy on silica gel (hexane/ethyl acetate 9:1) yielded 23 mg (65%) of **3** as red crystals. ^{1}H NMR (CDCl$_3$): 4.11 (s, 5 H, C$_5$H$_5$); 4.23 (apparent t, 2 H, C$_5$H$_4$); 4.38 (apparent t, 2 H, C$_5$H$_4$); 6.40 (s, 1 H, CH=). M.p. 283–284 (dec.) °C (ref.[2] gives 265–267 °C, ref.[14] 270 (dec.) °C). HR MS calculated for C$_{22}$H$_{20}$Fe$_2$ (M$^{\bullet +}$) 396.0264, found 396.0276.

Preparation of 1,2-Diferrocenylethane (4)

Pd/CaCO$_3$ (5 mole %) was placed into a flask and the flask was flushed several times with hydrogen. A solution of **1** (20 mg, 0.05 mmol) in dichloromethane (2 ml) was added and the mixture was stirred under hydrogen (1 atm) for 12 h. The catalyst was filtered off, the filtrate evaporated under reduced pressure, and the residue purified by flash chromatography on silica gel (hexane/ethyl acetate 9:1) to give **4** as red crystals (19.4 mg, 96%). ^{1}H NMR (CDCl$_3$): 2.54 (s, 2 H, CH$_2$); 4.05–4.07 (m, 4 H, C$_5$H$_4$); 4.10 (s, 5 H, C$_5$H$_5$). M.p. 201–202 (dec.) °C (refs[2,15] give 193–195 °C). HR MS calculated for C$_{22}$H$_{22}$Fe$_2$ (M$^{\bullet +}$) 398.0420, found 398.0434.

X-Ray Crystallography

Stucture determination for **1**: $C_{22}H_{18}Fe_2$ (M = 394.06 g mol^{-1}), monoclinic, $P2_1/c$ (No. 14), T = 150 K, a = 10.3629(4) Å, b = 10.2397(4) Å, c = 7.5776(4) Å; β = 90.763(3)°, V = 804.01(6) Å^3, Z = 2, D_c = 1.628 g ml^{-1} (red plate, 0.08 × 0.13 × 0.48 mm^3), 12 589 integrated, 1850 unique, and 1479 observed [$I > 2\sigma(I)$] diffractions (2θ$_{max}$ = 55°) numerically corrected for absorption [μ(MoKα) = 1.802 mm^{-1}, T_{min} = 0.769, T_{max} = 0.878, Nonius KappaCCD diffractometer]. Since the selected crystal exhibited pseudomerohedral twinning, mimicking a higher, orthorhombic symmetry of the diffraction pattern, the diffractions were corrected during the refinement for the contribution of the second part by using the twin operation

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

applied on (*hkl*). This yielded fractional contributions of the two components *ca* 0.905:0.095. The structure was solved by direct methods (SIR92)[16] and refined by weighted full-matrix least-squares on F^2 (SHELXL97)[17]. All non-hydrogen atoms were refined with anisotropic thermal motion parameters. The hydrogen atoms were included in theoretical positions (C–H 0.93 Å) and assigned U_{iso}(H) = 1.2 U_{eq}(C). Final R = 0.0425 and wR = 0.104 (observed diffractions), R = 0.0577 (all data); 110 parameters, goodness-of-fit 1.01, extremes on the residual electron density map +1.21 and –0.60 e Å^{-3}.

CCDC 221675 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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