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Preliminary communication

1,2-Diethynylferrocene

Uwe H.F. Bunz

Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55021 Mainz, Germany

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Abstract

Synthesis of 1,2-diethynylferrocene (**2**), 1,2-divinylferrocene (**3**) and 1-ethynyl-2-vinylferrocene (**5**) starting from ferrocene-1,2-dicarboxaldehyde (**1**) is reported.

Keywords: Iron; Alkyne; Ferrocene; Diyne

1. Introduction

The synthesis of complexes with π-ligands carrying ethynyl groups has become increasingly more important during the last five years [1–5]. This is due to the combination of attractive structural and/or electronic properties of the organometallic part and the ease of functionalization of the pendant alkyne group(s) [2]. Additionally, alkynylated complexes could be polymerized or oligomerized or undergo thermal rearrangements of the π-ligand [3]. Diethynylated complexes of π-bond cyclobutadienes (both 1,2- and 1,3-disubstituted) have been known for over fifteen years due to the elegant work of Fritch and Vollhardt [3] and more recently from the work in our own group [6]. However, although several monoalkynyl substituted Cp-complexes are known (and in the case of 1,1′-diethynyl substituted ferrocenes are prepared with relative ease) diethynyl substituted cyclopentadienes (complexed or uncomplexed) are hitherto unknown. This is even more surprising in view of the body of work carried out on Cp-systems as compared to the cyclobutadiene complexes. We wish to report here the synthesis of 1,2-diethynylferrocene, the first ferrocene carrying two alkynyl groups on one ring.

2. Results and discussion

Searching the literature revealed, that **1** [7] can be prepared in four steps from the commercially available N,N-dimethylaminomethylferrocene. It was reacted with the Corey-Fuchs-reagent [8] to give the desired diyne **2**, but only in 10%. In order to obtain larger quantities of **2** we explored a different route to **2**, treating **1** with "instant-ylide" (a commercially available mixture of (methyltriphenyl)phosphonium bromide and sodium amide) in THF to isolate **3** in 78% yield.

Complete bromination of **3** in dichloromethane (−78°C) afforded a sparingly soluble solid (95%) we assigned the structure **4**. It was formed as a mixture (ca. 2 : 1) of diastereomers (*dl* and *meso*) and the isomeric ratio was inferred from the line intensities of the resonances of the Cp-rings in the ^{13}C NMR and the very complicated ^{1}H NMR spectra. The more abundant is the less symmetric *dl* diastereomer; thus an assignment of the signals to the corresponding diastereomers is neither possible by ^{1}H NMR nor by ^{13}C NMR spectroscopy, with the exception of the signals of the intact Cp rings. Elemental analysis supports our proposal. Treatment of **4** with an excess of LDA at −78°C gave rise to the isolation of **3** in 85% yield instead of the formation of **2**. We assume that a nucleophilic attack of the LDA on the bromine substituents [9] had taken place (instead of elimination of HBr) leading back to **3**. The occurrence of this process could be a consequence of the high steric congestion in **4** which will promote the bromophilic reaction. Treatment of **4** with sodium amide in liquid ammonia yielded a mixture of two compounds which were separated by chromatography and have been identified by their NMR spectra as the hitherto unknown **5** (24%) and **2** (15%). The use of the sterically less congested amide ion (compared to LDA) appears to

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promote the elimination of HBr over the bromophilic substitution.

In order to obtain larger quantities of **2** and to avoid the occurrence of a bromophilic reaction we conducted a double Wittig-chloroolefination of **1** with $Ph_3P{=}CHCl$ (**6**) [10] and treated the raw product with KO^tBu in THF to effect double dehydrochlorination. Aqueous workup yielded 46% **2** (referred to **1**, average yielded 68% per step). The formation of **5** or other side products was not observed. The route described in this last paragraph is the method of choice for the preparation of **2**.

All three compounds **2**, **3** and **5** are obtained as dark orange viscous oils. While **2** and **3** are stable on the bench top for extended periods of time (**2** slowly solidifies), **5** decomposes over several weeks under air to an infusible and intractable material. In solution **4** is very sensitive and decomposes over a period of time > 2 h to a black insoluble and infusible material, while it is stable in the solid state for at least several days under ambient conditions.

First experiments to induce a Bergman-rearrangement [3,11] in **2** showed a complete decomposition of the starting material (195°C/48 h/decane/cyclohexadiene/sealed ampoule), but no occurrence of defined products.

In conclusion we have been able to develop a Wittig/dehydrohalogenation route to the hitherto unknown *ortho* diethynylferrocene **2**. In future publications we will report on the gas phase rearrangement and chemistry of **2**.

3. Experimental details

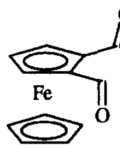
All reactions were carried out in flame dried glassware under inert conditions (N_2). The NMR spectra were taken at 200 MHz (^1H) and at 50 MHz (^{13}C) at ambient temperature on a Varian Gemini 200 spectrometer. IR spectra were taken on a Nicolet 320 FTIR spectrometer. Elemental analyses were performed in the Microanalytical Laboratory of the Institut für Organische Chemie der Universität Mainz. δ-values (NMR) are given in ppm.

3.1. 1,2-Divinylferrocene (3)

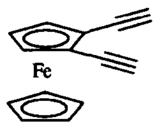
1 (1.47 g, 6.07 mmol) was added to a precooled (0°C) suspension of instant ylide (6.00 g, ca. 15 mmol, Aldrich) [12] in anhydrous THF (ca. 50 ml) contained in a 100 ml Schlenk tube. The reaction mixture was allowed to warm to 21°C and stirred for 18 h. Aqueous workup and distillation (0.01 Torr; bath 20–60°C) yields **3** (1.13 g 78%). Analytically pure **3** is obtained by chromatography over flash silica gel (pentane).–IR (KBr): 3086, 3008, 1623, 1409, 1277, 1120, 1106.–^1H NMR ($CDCl_3$): $\delta = 4.11$ (s, 5 H, Cp′–H), 4.34 (t, $J = 2.52$ Hz, 1 H, Cp–H), 4.57 (d, $J = 2.52$ Hz, 2 H, Cp–H), 5.19 (dd, $J_1 = 10.8$ Hz, $J_2 = 1.65$ Hz, 2 H, vinyl–H), 5.46 (dd, $J_1 = 17.5$ Hz, $J_2 = 1.65$ Hz, 2 H, vinyl–H), 6.72 (dd, $J_1 = 17.5$ Hz, $J_2 = 10.8$ Hz, 2 H, vinyl–H). ^{13}C NMR ($CDCl_3$): $\delta = 66.1$ (d, 2 C, Cp–C), 68.3 (d, Cp–C), 70.4 (d, 5 C, Cp′–C), 82.3 (s, Cp–C), 112.6 (t, 2 C, vinyl–C), 132.9 (d, 2 C, vinyl–C).–MS (EI, 70 eV): 238 (M^+), 236, 173, 172, 121, 115. $C_{14}H_{14}Fe$ (236.1) Calc. C 70.62; H 5.93. Found C 70.62; H 5.97.

3.2. Bromination of 1,2-divinylferrocene

3 (914 mg, 3.84 mmol) was dissolved in dichloromethane (ca. 50 ml) and the solution cooled to −78°C. To this solution was added a solution of bromine (1.19 g, 7.44 mmol) in dichloromethane (ca. 20 ml) over a period of ca. 20 min and the resulting mixture was stirred for 10 min at 21°C. The solvent was removed in vacuo to give 2.10 g of a dark almost insoluble crystalline mass which was used without further purification in the elimination experiment. To obtain a sample for analytical purposes, **4** (ca. 100 mg) was dissolved in dichloromethane (ca. 50 ml) and pentane (ca. 50 ml) was added until a turbid dispersion emerged. Filtration gave a yellow solution leaving a lemon yellow microcrystalline powder (ca. 95 mg) behind upon removal of the solvents which was used for all analytical purposes; **4** was obtained as a mixture of two diastereomers in the ratio of ca. 2 : 1, favoring the *dl*-pair over the *meso*-compound; 105°C dec.–IR (KBr): 3103, 3086, 2963, 1713, 1672, 1642, 1632, 1410, 1207,



1



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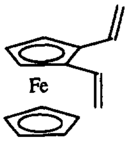

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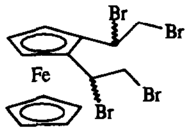

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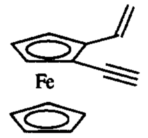

5

1174, 1119, 873, 851, 822.–^{13}C NMR (C_6D_6): $\delta = 36.8$, 37.2, 38.5 (3 d, CHBr–), 50.7, 51.3, 51.5 (3 t, CH_2Br), 66.1, 68.0, 68.7, 69.7, 69.9 (5 d, Cp-C) 70.9, 71.2 (2 d, Cp′-C), 85.3, 86.1, 87.7 (3 s, Cp-C).–MS (EI, 70 eV): 396 (M^+-2Br), 316, 238, 236. $C_{14}H_{14}FeBr_2$ (557.7) Calc. C 30.15; H 2.53; Br 57.30. Found C 29.91; H 2.48; Br 56.84.

3.3. *1,2-Diethynylferrocene (2) and 1-ethynyl-2-vinylferrocene (5)*

A sodium amide suspension was prepared from sodium (3.00 g, 125 mmol) and a trace of $FeCl_2$ in liquid ammonia (ca. 100 ml). A suspension of the crude **4** (3.23 g, 5.91 mmol) in anhydrous THF (ca. 15 ml) was added to the base and stirred for 2 h under reflux. Aqueous extractive workup (pentane) and chromatography of the residue over flash silica gel (pentane : ether 9 : 1) yielded 337 mg (24%) **5** as first fraction, followed by 209 mg (15% of **2**.- **5**: IR (KBr): 3299, 3094, 2105, 1628, 1265, 1106, 1037.–^{1}H NMR ($CDCl_3$): $\delta = 2.91$ (s, 1 H, alkyne–H), 4.17 (s, 5 H, Cp′–H), 4.26 (t, $J = 2.56$ Hz, 1 H, Cp-H), 4.53 (m, 2 H, Cp–H), 5.21 (dd, $J_1 = 10.9$ Hz, $J_2 = 1.51$ Hz, 1 H, vinyl–H), 5.62 (dd, $J_1 = 17.6$ Hz, $J_2 = 1.51$ Hz, 1 H, vinyl–H), 6.69 (dd, $J_1 = 17.6$ Hz, $J_2 = 10.9$ Hz, 1 H, vinyl-H).–^{13}C NMR ($CDCl_3$): $\delta = 63.8$ (s, Cp–C), 65.8 (d, Cp–C), 68.5 (d, Cp–C), 71.3 (d, 5 C, Cp′–C), 72.3 (d, Cp–C) 76.2 (d, alkyne–C), 80.6 (s, alkyne–C), 85.2 (s, Cp–C) 112.7 (t, vinyl–CH_2) 132.7 (d, vinyl–CH).- MS (EI, 70 eV): 236 (M^+), 121, 115, 84. $C_{14}H_{12}Fe$ (236.1). **2**: mp 46°C.–IR (KBr): 3287, 3097, 2112, 1411, 1260, 1245, 1106, 1091.–^{1}H NMR ($CDCl_3$): $\delta = 2.92$ (s, 2 H, alkyne–H), 4.21 (t, $J = 2.62$ Hz, 1 H, Cp–H), 4.24 (s, 5 H, Cp′–H), 4.53 (t, $J = 2.62$ Hz, 2 H, Cp–H). ^{13}C NMR ($CDCl_3$): $\delta = 67.5$ (s, Cp–C), 68.7 (d, C, Cp–C), 72.1 (d, 7 C, Cp′–C, Cp–C), 76.2 (d, alkyne–CH) 80.6 (s, alkyne–C). MS (EI, 70 eV): 234 (M^+), 179, 152, 121. High resolution MS for $C_{14}H_{10}Fe$: Calc. 234.0132, Found 234.0136. $C_{14}H_{12}Fe$ (234.1) Calc. C 71.83; H 4.31. Found C 71.82; H 4.42.

3.4. *1,2-Diethynylferrocene (2) by the Corey-Fuchs-method*

Triphenylphosphine (4.28 g, 16.3 mmol), carbon tetrabromide (5.41 g, 16.3 mmol) and zinc dust (1.07 g, 16.3 mmol) were mixed in anhydrous dichloromethane (ca. 50 ml) and stirred for 18 h. **1** (808 mg, 3.34 mmol), was added and the mixture stirred for 3 h. Precipitation of the reaction mixture into pentane, removal of the formed phosphine oxide by filtration and subsequent evaporation of the solvent in vacuo produced a dark red mass, which was dissolved in dry THF and treated with BuLi (10.0 ml, 16.0 mmol) at −78°C for 30 min. After warming to 21°C and stirring for 1 h, aqueous workup and distillation of the raw product (0.01 Torr/bath 40°C–80°C) gave rise to the isolation of 82 mg (10%) spectroscopically pure **2**.

3.5. *1,2-Diethynylferrocene (2) by Wittig-chloroolefination and subsequent HCl elimination*

Ylide **6** was prepared by treating a slurry of (chloromethyl)triphenylphosphoniumiodide (5.00 g, 11.4 mmol) [11] with BuLi (7.13 ml, 11.4 mmol) in THF (ca. 50 ml, 0°C). At 0°C **1** (1.00 g, 4.13 mmol) was added. The reaction mixture was stirred over night at room temperature and worked up by precipitation into ca. 1 l pentane to remove triphenylphosphine oxide. The obtained dark oil was filtered over flash silica gel (3 × 7 cm; pentane as eluent) to obtain 983 mg of a yellow oil. This product was dissolved in anhydrous THF (ca. 50 ml) and treated at room temperature with KOtBu (2.24 g, 20.0 mmol) for 18 h. The reaction mixture was diluted with 300 ml pentane and hydrolyzed. Chromatography over flash silica gel (1 : 9 ether/pentane) gave rise to the isolation of **2** (453 mg, 46%). Attempts to perform the same reaction in a one pot procedure yielded only 36% of **2**.

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