# Asymmetric Ethynes. Syntheses of Ethynylferrocene Paradigms

Johann Polin<sup>a</sup>, Herwig Schottenberger<sup>b</sup>, Karl Eberhard Schwarzhans<sup>b,\*</sup>

<sup>a</sup> Dipartimento di Chimica "G. Ciamician", Universitá degli Studi di Bologna, Via Selmi 2, I-40126 Bologna, Italy

<sup>b</sup> Institut für Allgemeine, Anorganische und Theoretische Chemie, Universität Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria

Dedicated to Prof. Dr. H. P. Fritz

Z. Naturforsch. 51 b, 1683-1690 (1996); received June 10, 1996

Ethynylferrocene, Donor-Acceptor Systems, Coupling Reactions

Synthetic methods to bifunctional ethynes have been examined. Direct ethynylation, the Stephens-Castro reaction, the Pd-catalysed Hagihara coupling, transmetalation reactions and nucleophilic additions have been evaluated in the preparation of substituted ferrocenylethynes with intended use of these materials in electrochemical and nonlinear optical investigations. Asymmetric ferrocenylethynes are promising candidates for applications in contemporary materials science. Synthetically, 1,4-bis(ferrocenylethynylene)benzene (1), 1,3,5-tris(ferrocenylethynylene)benzene (2), and 9,10-bis(ferrocenylethynylene)anthracene (3) are obtained in high yields, whereas 4-ferrocenylethynylene-2,3,5,6-tetrafluorostyrene (4) and potassium (ferrocenylethynylene)triphenyl borate (5) are accessible in only moderate yields. Further extension of this chemistry to additional heteronuclear bimetallic coordination compounds has been attempted, but without success due to severe difficulties in both preparation and characterization of these materials.

# Introduction

The C $\equiv$ C carbon-carbon triple bond established itself as a versatile organic building-block that enables well-defined molecular structures particularly when combined with aryl substituents. The synthetic potential of ethynes and ethynylarenes offers a vast variability ranging from direct ethynylation and metal-mediated coupling reactions to cyclo- and polymerization [1]. Acetylene based systems find wide utilization in LCs [2], polymer LEDs [3], high performance thermosets and carbon-carbon composites [4]. Suitable functionalization leads to structures with applications in electro- [5] and magnetochemical [6] devices, to NLO-phores with  $\chi^{(2)}$  and  $\chi^{(3)}$  response [7], to supramolecular components for photonics [8] as well as to chemicals with significant bioactivity [9], comprising derivatives such as HIV reverse transcriptase inhibitors [9e]. Most of the aforementioned utilizations profit from the sp-conjugation of acetylenic spacers which allows intramolecular interactions like charge averaging or energy and electron transfer. The enforced rigidy of this structural element, on the other hand, is getting important in advanced molecular architectures. For instance, organic networks mimicing diamondoide or zeolithic arrays are accessible by self-assembling of acetylene based templates [10]. Consequently, organic solid state chemistry significantly benefits from the electronic and structural particularities of this molecular constituent.

This paper reports on the synthesis of bifunctional ethynes with emphasis on ethynylferrocenes, applying various organometallic substitution reactions. The target materials are designed for basic electrochemical and hyperpolarizability studies.

# Diarylacetylenes in Nonlinear Optics and Molecular Electronics

For the application-oriented construction of target compounds with acetylenic bridging ligands three obvious candidates can be envisaged. First, the title compound ethynylferrocene itself, second, ferrocenyl-4,4'-disubstituted tolane derivatives, and third, ferrocenyl-ethynyl-2,2'-bipyridyl metal complexes with the respective potential for uses in the fields of nonlinear optics and molecular electronics.

0939–5075/96/1200–1683 \$ 06.00 © 1996 Verlag der Zeitschrift für Naturforschung. All rights reserved. K

<sup>\*</sup> Reprint requests to Prof. Dr. K. E. Schwarzhans.

Tolane based donor-acceptor molecules have excessively been discussed as materials for nonlinear optics because of their structural and electronic features [11]. Systematic theoretical studies, SHG, EFISH and THG measurements of 4,4'disubstituted tolanes with numerous different substituents give evidence that both suszeptibilities and hyperpolarizabilities are at best moderate. Consequently, the significant enhancement of nonlinear optical responses necessitates new concepts. Synthetical approaches which take this demand into account comprise the integration of novel substituents such as inductive and cationic acceptors, replacing diphenylacetylenes by (phenylethynylene)pyridinium links, (and use in LB films [12] or superlattice environments [13], respectively), as well as the preparation of oligo(ethynylenephenylene) spacers [7b,e, 14] and polymers with pendent NLO-phores [15]. Since ferrocene derivatives represent the most versatile class of organometallic systems in the field of nonlinear optics, the investigation of (ferrocenylethynylene)phenylenes instead of diphenylacetylenes appears inviting. The donor-acceptor compound 4 for instance has been designed as monomer precursor to branched polyvinyls.

2,2'-Bipyridyl derivatives with ethynyl substituents at their 4,4'- or 5,5'-positions rather than 6,6' (for sterical reasons in coordination compounds) and, to some extent, cognate terpyridines with less favorable chelating characteristics as well as rigid 1,10-phenanthrolines find continued interests in molecular electronics. Corresponding mono-, di- and polynuclear Ru(II) and Os(II) complexes allow photoinduced energy and electron transfer processes [16]. Properly designed systems permit the manufacture of homo- and heteronuclear coordination complexes with tunable redox and luminescence properties.

Bi- and termetallocenes such as compounds **1**, **2** and **3** are likely suited for basic electrochemical investigations. Furthermore, 1,3,5-tris(phenylethynylene)benzene and 1,3,5-tris(ferrocenylvinylene)benzene analogues of compound **2** have recently been reported as potential NLO-phores [17].

## Ethynylferrocene derivatives

The Vilsmeier reaction has been recognized to be a highly efficient synthetic route towards ethynylferrocene [18] which represents an economic and versatile module. Alternative synthetic methods are more tedious and generally more expensive. Ferrocenylacetylenes have soon been recognized as potential starting materials to more complex organometallics and macromolecular systems owing to the terminal ethyne which enables a variety of distinct coupling reactions. Diferrocenylacetylene, [2.2]ferrocenophane-1,13-diyne (both being widely used in intervalence transfer studies [1b]), (ferrocenylethynylene)benzene and ferrocenyl-1naphthylacetylene are well-known derivatives [5a, 18a, 19]. Subsequent preparation of heteronuclear (ferrocenylethynylene)cobaltocenium salts [20] and further electrochemical investigations complement the range of acetylene-bridged bimetallocenes. As mentioned above, the proposed bis- and tris(ferrocenylethynylene) arenes 1, 2 and 3 are of comparable interest with regard to intervalence transfer studies.

Organometallic chromophores are quite interesting for nonlinear optics because they may exhibit (a) MLCT and LMCT interactions, (b) redox reversibility which makes the metal center an extremely strong acceptor or donor, and (c) generally low-energy excited states with dipole moments significantly different from their groundstate dipole moments. These properties give rise to large optical nonlinearities. Ionic species offer additional important features such as counterion metathesis to obtain higher nonlinear optical responses and non-centrosymmetric structures, the basic requirement for second-order NLO materials, as well as favorable solubility and processibility characteristics. The intense color of certain systems, however, causes transparency problems and nonlinear optical investigation of salts and mixed-valency metal complexes in solution is restricted to the Hyper-Rayleigh Scattering technique (HSR), which is the only method available for determining the  $\beta$  values of such compounds [21]. Consequently, acceptor substituted ferrocenylethynes like 4-(ferrocenylethynylene)cyanobenzene [7a, 22], 4-(ferrocenylethynylene)acetylbenzene [23], 4-(ferrocenylethynylene)nitrobenzene [22, 23], (ferrocenylethynylene)dimesitylborane [7c] and 1,8-bis(ferrocenyl)octatetrayne [7d] can be found among recently discussed NLOphores. However, 4-ferrocenylethynylene-2,3,5,6tetrafluorostyrene 4 and potassium (ferrocenyl-



Table I. Chart of selected ethynylferrocene derivatives.

ethynylene)triphenyl borate **5** have been prepared to meet several of the more important requirements for  $\chi^{(2)}$  materials. Synthesis and characterization of (ferrocenylethynylene)benzene chromium tricarbonyl and pentamethylcyclopentadienyl ruthenium complexes, on the other hand, failed. These findings stress the necessity of convenient accessibility as an additional demand for purposive materials. Synthetic approaches towards the aforementioned novel ferrocenylethynyl derivatives **1-5** will therefore be discussed in the following section with emphasis on the most efficient routes.

## **Results and Discussion**

An early approach to (ferrocenylethynylene)arenes by Stephens and Castro, i. e. coupling of cuproacetylides with haloarenes in pyridine, yielded materials such as diferrocenylacetylene, [2.2]ferrocenophane-1,13-diyne and ferrocenyl-1naphthylacetylene [18a, 19, 24]. We tried the coupling of cuprous ferrocenylacetylide with 1,4-dibromobenzene and 9,10-dibromoanthracene which yielded 1,4-bis(ferrocenylethynylene)benzene 1 and 9,10-bis(ferrocenylethynylene)anthracene 3. However, purification and separation from 1,4diferrocenyl-1,3-butadiyne, the byproduct which results from undesired dimerization, turned out to be difficult and the yields were not satisfactory. The Hagihara coupling, i.e. the Pd/Cucatalysed reaction of terminal ethynes with haloarenes in amine solvents, has already been reported to be favorable in the preparation of diferrocenylacetylene, 1,3,5-tris(phenylethynylene)benzene and 9,10-diethynylanthracene derivatives, respectively [8a,d, 17a, 25]. Even the synthesis of (ferrocenylethynylene)benzene and (ferrocenvlvinylene)benzene derivatives has been reported to profit from Pd-catalysed reaction conditions according to Hagihara and Heck, respectively [5b, 17b, 26]. Accordingly, the Pd/Cu-mediated preparation of 1 and 2 from commercially available bromobenzene precursors proceeded smooth with yields up to 95 %. However, considerable amounts of monosubstituted (9-bromo-10-ferrocenvlethvnvlene)anthracene were obtained in the synthesis of 3 under quite mild conditions, which indicates the necessity of elevated temperatures and elongated reaction times in this case of twofold substitution.

Furthermore, it was among the aims to enrich the spectrum of heterobimetallic acetylenes by additional coordination complexes. However, the synthesis of novel systems, namely  $\eta^6$ -(ferrocenylethynylene)benzene chromium tricarbonyl,  $\eta^6$ -(ferrocenylethynylene)-p-chlorobenzene chromium tricarbonyl and ( $\eta^5$ -pentamethylcyclopentadienyl)ruthenium  $[\eta^6$ -(ferrocenylethynylene)benzene] triflate under Hagihara conditions from appropriate precursors failed. Insufficient coupling and/or ambigous characterization of the target compounds prohibited access to these asymmetric ethynes, although the large-scale preparation of respective starting materials ( $\eta^{6}$ -4-bromochlorobenzene chromium tricarbonyl, ( $\eta^5$ -pentamethylcyclopentadienyl)ruthenium( $\eta^6$ -iodobenzene) triflate) proved possible.

The synthesis of 9,10-bis(ferrocenylethynylene)anthracene gave evidence that the nucleophilic addition method that utilizes anthraquinone and



Fig. 1. Coupling reactions of ethynylferrocene to target compounds **1-5**: a) 1,4-diiodobenzene;  $(Ph_3P)_2PdCl_2/Cu(I)I/({}^{i}Pr)_2NH$ , 18 h, r.t.; b) 1,3,5-tribromobenzene;  $(Ph_3P)_2PdCl_2/Cu(I)I/({}^{i}Pr)_2NH$ , 6 d, RF; c) anthraquinone; 1. *n*-BuLi/THF, -78°C, 2. TMEDA/1,4-dioxane, 18 h, RF, 3. ZnCl<sub>2</sub> · 2 H<sub>2</sub>O/HOAc/1,4-dioxane, 60 min, r.t.; d) 2,3,4,5,6-pentafluorostyrene; *n*-BuLi/THF, -78°C, 2 h, r.t.; e) triphenylborane; 1. *n*-BuLi/THF, -78°C, 18 h, r.t., 2. KCl, H<sub>2</sub>O; f) ( $\eta^5$ -pentamethylcyclopentadienyl)ruthenium( $\eta^6$ -iodobenzene); (Ph<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub>/Cu(I)I/( ${}^{i}Pr$ )<sub>2</sub>NH, 14 h, RF; g)  $\eta^6$ -4-bromochlorobenzene chromium tricarbonyl; (Ph<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub>/Cu(I)I/( ${}^{i}Pr$ )<sub>2</sub>NH, 4 d, r.t.

lithium acetylides as reaction partners is quite efficient and competes well with the palladium catalysed approach. The addition-elimination reaction generally proceeds without problems and yielded compound **3** with 77%. The lanthanide mediated version of the carbonyl alkynylation [27] has not been tested but could certainly be advantageous.

One of the most straightforward preparation methods to diarylethynes is the reaction of monosubstituted ethynes with susceptible arenes via *in situ* generation of lithium acetylides. This strategy proved successful in the synthesis of (ferrocenylethynylene)cobaltocenium hexafluorophosphate and related systems [7b, 20], as well as in the preparation of ethynylpentafluorobenzenes [28]. Further substitution in monosubstituted perfluorobenzenes predominantly occurs *in para* position [28]. Thus, it was of interest to study the reaction of ethynylferrocene with 2,3,4,5,6-pentafluorostyrene, which is commercially available and guarantees convenient access to 4-ferrocenylethynylene-2,3,5,6-tetrafluorostyrene **4**. The styrene unit enables polymerization which is particularly interesting as the favorable inductive effect of fluoro substituents in perfluoroarenes and the acetylene bridge promise remarkable nonlinear optical activity.

Even ethynyltriphenyl borates and phosphinoboratoacetylenes have been prepared by direct ethynylation [29]. Both materials, the zwitterionic (diphenylmethylphosphino)triphenylboratoacetylene [29b, 30], and (ferrocenylethynylene)dimesitylborane [7c], have been proposed as NLOphores besides transparent ammonium/borate zwitterions [31]. On the other hand, combination of ethynylferrocene with triphenylborane vielded potassium (ferrocenylethynylene)triphenyl borate 5, an additional boron containing compound with distinct advantages for second order nonlinear optics. Following the synthetic concepts, the most desirable material would be (cobaltoceniumethynylene)triphenyl borate. However, we were vet not able to prepare this zwitterionic D/A complex.

The preparation of lithium ferrocenylacetylide and subsequent transmetallation finally has been reported as method of choice in the Pdcatalysed coupling to squaric acid derivatives such as 3-ferrocenyl-4-(ferrocenylethynylene)cyclobut-3-en-1,2-dione and 3,4-bis(ferrocenylethynylene)cyclobut-3-en-1,2-dione [32], which represent an additional class of ethyne bridged D/A-systems and contribute to the more classical donor-acceptor systems as 4-(ferrocenylethynylene)nitrobenzene, 4-(ferrocenylethynylene)cyanobenzene and 4-(ferrocenylethynylene)acetylbenzene [22, 23].

#### **Experimental Section**

All experiments were carried out under an inert atmosphere using standard Schlenk technique unless otherwise indicated. THF was distilled under argon from sodium benzophenone and reagent grade dichloromethane from calcium hydride. Starting materials were used as purchased without further purification or prepared according to literature procedures and checked for purity. Silica for column chromatography was purchased from Fluka. The analytical equipment for spectroscopic characterization comprises: Bruker AM 300 and AM 200 (<sup>1</sup>H NMR, <sup>13</sup>C NMR;  $\delta$  [ppm] *vs.* TMS); Nicolet 510M FT-IR (IR;  $\nu$ [cm<sup>-1</sup>]); CH-7 MAT (EI, 70 eV) and Finnigan MAT 90 (MS); Hitachi U 2000 (UV-VIS;  $\lambda_{max}$  [nm]).

## 1,4-Bis(ferrocenylethynylene)benzene (1)

Ethynylferrocene (0.84 g, 4.0 mmol) and 1,4-diiodobenzene (0.66 g, 2.0 mmol) were suspended in diisopropylamine (15 ml) under argon. The system was stirred for a few minutes, bis(triphenylphosphine)palladium(II) chloride (140 mg, 0.2 mmol) and copper(I) iodide (76.0 mg, 0.4 mmol) were added, and the system, which soon darkens, was stirred at room temperature for 18 h.

The reaction mixture was filtered by suction through a sintered glass frit (G3) and successively washed with small amounts of diisopropylamine, hexane and diethylether. The residue was taken up in THF, filtered again and the solvent evaporated under reduced pressure. The product was dried in vacuo. Pure 1,4bis(ferrocenylethynylene)benzene (0.93 g, 1.9 mmol, 94%) was obtained. MS: m/z = 493 (100%).



Fig. 2. MS 1,4-Bis(ferrocenylethynylene)benzene.

#### 1,3,5-Tris(ferrocenylethynylene)benzene (2)

1,3,5-Tribromobenzene (31.5 mg, 1.0 mmol) was dissolved in diisopropylamine (5 ml). Bis(triphenyl-phosphine)palladium(II) chloride (3.5 mg, 0.05 mmol) and copper(I) iodide (19 mg, 0.1 mmol) were added, and the system was stirred at room temperature. Ethynylferrocene (0.693 g, 3.3 mmol) was dissolved in diisopropyl-amine (15 ml) and slowly added to the reaction mixture by means of a dropping funnel. The solution darkens immediately. The dropping funnel was then replaced by a reflux condenser and the system stirred under reflux. The color of the reaction mixture turned brown after 3 h when TLC showed 3 spots; after 2 d only two TLC-spots remained visible. The reaction was terminated after 6 d, when coupling was completed.

The reaction mixture was filtered through a sintered glass frit and carefully washed with diisopropylamine.

The residue was taken up in THF and combined with small amounts of product that could be isolated from the mother liquor. The solvent was removed under reduced pressure and 1,3,5-tris(ferrocenylethynylene)benzene (0.66 g, 94%) was obtained.

IR (KBr): 3100 w, 2970 s, 2850 m, 2725 w, 2220 m  $\nu$ (C $\equiv$ C), 1760 m, b, 1560 m, b, 1480 w, 1420 w, 1400 w, 1120 s, 1045 w, 1030 m, 1003 s, 970 s, 878 s, 820 s, b, 758 w, 682 w. - <sup>1</sup>H NMR (CCl<sub>4</sub>): 7.53 s, 3H, 4.40, m, 6H, 4.18 m, 21H. - <sup>13</sup>C NMR (CCl<sub>4</sub>) 174.4, 132.5, 71.0, 69.7, 68.4. - MS: *m/z* = 702 (M<sup>++</sup>). - UV/Vis (CCl<sub>4</sub>, 10<sup>-6</sup> mol/ml): 238, 262, 306, 448.

#### 9,10-Bis-(ferrocenylethynylene)anthracene (3)

Ethynylferrocene (1.05 g, 5.0 mmol) was dissolved in dry THF (25 ml). The solution was cooled to -78°C and *n*-butyllithium (2.4 M solution in *n*-hexane, 2.1 ml) was slowly added. The mixture was warmed to room temperature and stirred for 60 min. After removal of solvents the remaining orange residue was dissolved in dry 1,4dioxane (30 ml). Anthraquinone (0.52 g, 2.5 mmol) and TMEDA (5 ml) were added to the solution and the system was refluxed for 18 h. The color of the reaction mixture changed from red to olive brown.

Precipitation of the orange intermediate glycol isomer was achieved by adding 100 ml of water. The crude product was filtered (G3) and remaining residues in the flask were extracted with dichloro methane. The combined crops were purified by column chromatography (Silica G-60741, 5x15 cm, 1. *n*-hexane, 2. diethylether). The hexane fraction was discarded whereas the ether fraction yielded the pure intermediate almost quantitatively after removing the solvent and drying.

A flask was charged under inert atmosphere with tin(II) chloride dihydrate (68 mg, 0.4 mmol) and acetic acid (50 %, 30 ml). The intermediate glycols (251 mg, 0.4 mmol) were dissolved in dry 1,4-dioxane (30 ml) and slowly added to the tin chloride solution by means of a dropping funnel. The color of the solution turned red with formation of a precipitate. The reaction was terminated after 60 min, the system filtered and the residue was washed with water and dried. The product was taken up in small amounts of dichloro methane and purified by column chromatography (Silica G-60742, 4x40 cm, *n*-pentane/diethylether 50:50). The eluent was removed and the product dried. 9,10-Bis(ferrocenylethynylene)-anthracene (0.183 g, 77%) was obtained as a deep purple powder.

IR (KBr): 3091 w, 2964 w, 2198 m, 1775 w, 1725 w, 1652 w, 1621 w, 1436 w, 1410 w, 1370 m, 1170 w, 1106 s, 1064 m, 1003 s, 818 s, 753 s, 642 s, 529 w, 496 s. - MS: *m*/*z* = 594.

#### 4-Ferrocenylethynylene-2,3,5,6-tetrafluorostyrene (4)

Ethynylferrocene (0.5 g, 2.4 mmol) was dissolved in THF (20 ml) and the system cooled to -78°C. *n*-Butyllithium (2.0 M solution in *n*-pentane, 1.2 ml, 2.4 mmol) was added and the solution stirred for 1 h while rising the temperature to r.t..

2,3,4,5,6-Pentafluorostyrene (0.36 ml, 2.6 mmol) was slowly added and the system stirred for 2 h at room temperature. The color of the reaction mixture changed into an intense red. The solution was concentrated to remove solvent and unreacted pentafluorostyrene. The brownish-red residue was taken up in dry n-hexane and stirred overnight. The solution was concentrated and the product purified by column chromatography (Silica G-60741, 220-440 mesh, 3x60 cm, n-hexane/diethyl ether 70:30). An orange band and 120 mg of a red oil were isolated. The degree of purity of fraction 1 could be increased by a second chromatographic separation (Silica G-60741, 220-440 mesh, 5x60 cm, n-hexan/diethyl ether 50:50) which yielded 4-ferrocenylethynylene-2,3,5,6-tetrafluorostyrene (0.55 g, 59%). Fraction 2 contained low-molecular weight oligomers with MS-peaks at 441, 556 and 614.

IR (KBr): 3099 m, 3035 w, 2934 m, 2856 m, 2234 m, 1648 m, 1476 s, 1418 m, 1300 m, 1273 w, 1161 m, 1043 w, 955 s, 878 w, 822 s, 772 w, 484 s. - <sup>1</sup>H NMR (CDCl<sub>3</sub>): 6.61 dxd, 1H, 5.05 d, 1H (J = 17.7 Hz), 5.64 d, 1H (J = 11.6 Hz), 4.48 "t", 2H, 4.22 "t", 2H, 4.17 s, 5H. - <sup>13</sup>C NMR (CDCl<sub>3</sub>): 123.9, 122.2, 71.7, 70.0, 69.4. - MS: m/z = 383 M<sup>+</sup> (100%).

### Potassium (ferrocenylethynylene)triphenyl borate (5)

*Triphenylborane* [33]: Sodium tetraphenyl borate (20,0 g, 58,4 mmol) was dissolved in hot water (300 ml) and cooled to room temperature with stirring. A second solution was prepared from aqueous trimethylamine solution (15 %, 26.7 ml) and concentrated HCl (21.4 ml, 257 mmol). The solutions were combined with spontaneous formation of white trimethylammonium tetraphenyl borate [NH(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>[B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>]<sup>-</sup>. The system was vigorously stirred for 5 min and the precipitate filtered and dried. The white ammonium salt was pyrolized by slowly rising the temperature to 160°C to remove trimethylamine and benzene before collecting the pure product. Triphenylborane was obtained in 80% yield as white crystals and stored under argon at 4°C.

Potassium (ferrocenylethynylene)triphenyl borate (in analogy to the protocol of [29a]): Ethynylferrocene (1.05 g, 5.0 mmol) was dissolved in dry THF (25 ml) under argon. The system was cooled to -78°C and treated with

*n*-butyllithium (2.4 M solution in *n*-hexane, 2.1 ml, 5.0 mmol). After stirring for 90 min the solution was combined with triphenylborane (1.16 g, 4.8 mmol) in THF (50 ml). The cooling-bath was removed after 30 min and stirring was continued for further 18 h at room temperature.

The solvent was removed and the residue taken up in water. The mixture was extracted with *n*-hexane until the organic phase remained almost colorless. The aqueous phase was combined with a solution of potassium chloride (1.17 g, 15.7 mmol) in water (50 ml) to precipitate potassium borate. The flaky product was isolated by suction through a sintered glass frit, washed with water and dried. Potassium (ferrocenylethynylene)triphenyl borate (0.68 g, 28%) was obtained as yellow-orange powder.

IR (KBr): 3060 w, 2155 w, 1592 w, 1580 w, 1480 m, 1430 m, 1262 w, 1154 m, 1106 s, 1026 m, 1001 m, 945 m, 818 s, 764 m, 751 s, 739 s, 616 m, 596 m, 538 m, 486 s, 452 m. - <sup>1</sup>H NMR (CD<sub>3</sub>CN): 7.36 d, 6H (J = 8 Hz), 7.00 t, 6H (J = 8 Hz), 6.87 t, 3H (J = 8 Hz), 4.24 "t", 2H (J = 4 Hz), 4.16 s, 5H, 4.04 "t", 2H (J = 4 Hz). - <sup>13</sup>C NMR (CD<sub>3</sub>CN): 135.9, 131.4, 126.7, 89.1 (C $\equiv$ C), 71.2, 70.8, 70.2, 67.8. - MS: m/z = 451 (C<sub>30</sub>H<sub>24</sub>BFe, 100%). - UV/Vis (CCl<sub>4</sub>, 10<sup>-6</sup> mol/ml): 284, 444.

- [1] L. Brandsma, Preparative Acetylenic Chemistry, Elsevier, 2nd Ed., Amsterdam (1988).
- [2] a) R. Eidenschink, Angew. Chem. Adv. Mater. 101, 1454 (1989);

b) H. Bengs, M. Ebert, O. Karthaus, B. Kohne, K. Praefcke, H. Ringsdorf, J. H. Wendorff, R. Wüstefeld, Adv. Mater. 2, 141 (1990);
c) J. S. Moore, J. Zhang, Z. Wu, D. Venkataraman, S. Lee, Macromol. Symp. 77, 295 (1994).

- [3] a) T. Yamamoto, Prog. Polym. Sci. 17, 1153 (1992);
  b) T. Yamamoto, M. Takagi, K. Kizu, T. Maruyama, K. Kubota, H. Kanbara, T. Kurihara, T. Kaino, J. Chem. Soc., Chem. Commun. 797 (1993);
  c) A. P. Davey, S. Elliot, O. OConnor, W. Blau, J. Chem. Soc., Chem. Commun. 1433 (1995).
- [4] a) H. Kouzai, T. Masuda, T. Higashimura, Polymer 35, 4920 (1994);

b) S. V. Lindeman, Y. T. Struchkov, I. A. Khotina, V.N. Mikhailov, A. L. Rusanov, Russ. Chem. Bull. 43, 1873 (1994);

c) T. Takekoshi, J. M. Terry, Polymer 35, 4874 (1994);

d) T. M. Miller, T. X. Neenan, E. W. Kwock, S. M. Stein, Macromol. Symp. **77**, 35 (1994);

e) M. Strukelj, M. Paventi, A. S. Hay, Macromol. Symp. **77**, 369 (1994);

f) K. M. Jones, T. M. Keller, Polymer 36, 187 (1995).

## Conclusion

The synthesis of asymmetric acetylenes and ferrocenyl acetylenic donor/acceptor systems with perfluorinated arenes or arvl borates as the acceptor components is reported, using the easily accessible ethynylferrocene as key starting material. Bi- and termetallocenes are prepared by means of the well-established Hagihara coupling, whereas the fluoroarene and phenyl borate acceptor containing systems are accessible by nucleophilic substitution and nucleophilic addition, respectively. The latter materials introduce both inductive acceptor and covalently bonded anionic terminal functionalities with distinct advantages in ferrocene based NLO-phores, and contribute to the prevailingly studied classical organic functional groups as generally discussed in many tolane based structures. Further conceptual development towards molecular composites from these representatives gives rise to innovative and quite efficient materials with application in the fields of molecular electronics and photonics.

## Acknowledgements

This research was supported by the Fonds zur Förderung der wissenschaftlichen Forschung, Vienna, Austria (Project 10182 MOB).

[5] a) C. Le Vanda, K. Bechgaard, D. Cowan, J. Org. Chem. 41, 2700 (1976);

b) R. P. Hsung, C. E. D. Chidsay, L. R. Sita, Organometallics **14**, 4808 (1995).

- [6] a) H. Iwamura, Pure Appl. Chem. 65, 57 (1993);
  b) R. Saf, D. Hengg, K. Hummel, K. Gatterer, H. P. Fritzer, Polymer 34, 2680 (1993).
- [7] a) H. S. Nalwa, Appl. Organomet. Chem. 5, 349 (1991);

b) H. Nock, M. Buchmeiser, J. Polin, J. Lukasser, P. Jaitner, H. Schottenberger, Mol. Cryst. Liq. Cryst. **235**, 237 (1993);

c) Z. Yuan, N: J. Taylor, Y. Sun, T. B. Marder, J. Organomet. Chem. **449**, 27 (1993);

d) Z. Yuan, G. Stringer, I. R. Jobe, D. Kreller,
K. Scott, L. Koch, N. J. Taylor, T. B. Marder, J.
Organomet. Chem. 452, 115 (1993);
a) I. Polin, M. Buchmaiser, H. Nock, H. Schotten,

e) J. Polin, M. Buchmeiser, H. Nock, H. Schottenberger, Mol. Cryst. Liq. Cryst., in press.

- [8] a) A. V. Piskunov, A. A. Moroz, M. S. Shvartsberg, Izv. Akad. Nauk. SSSR, Ser. Khim 6, 1441 (1990);
  b) H. Takalo, E. Hänninen, J. Kankare, Helv. Chim. Acta 76, 877 (1993);
  - c) Z. Xu, J. S. Moore, Acta Polymer 45, 83 (1994);
    d) P. Nguyen, S. Todd, D. Van den Biggelaar, N. J. Taylor, T. B. Marder, F. Wittmann, R. H. Friend, Synlett 299 (1994).

[9] a) Y. Hatanaka, K. Matsui, T. Hiyama, Tetrahedron Lett. 30, 2403 (1989);

b) F. Freeman, S. H. L. Kim, J. Org. Chem. **58**, 2317 (1993);

c) J. A. Haugan, S. Liaaen-Jensen, Acta Chem. Scand. **48**, 899 (1994);

d) B. König, P. Bubenitschek, P. G. Jones, Liebigs Ann. 195 (1995);

- e) M. A. Huffman, N. Yasuda, A. E. DeCamp, E. J. J. Grabowski, J. Org. Chem. **60**, 1590 (1995).
- [10] a) Y. Ducharme, J. D. Wuest, J. Org. Chem. 53, 5787 (1988);

b) F. Persico, J. D. Wuest, J. Org. Chem. 58, 95 (1993);

c) E. Fan, J. Yang, S. J. Geib, C. Vicent, F. Garcia-Tellado, P. Tecilla, A. D. Hamilton, Macromol. Symp. 77, 209 (1994);

d) X. Wang, M. Simard, J. D. Wuest, J. Am. Chem. Soc. **116**, 12119 (1994);

e) Z. Wu, J. S. Moore, Polym. Prepr. **34/1**, 122 (1993);

f) J. Zhang, J. S. Moore, Polym. Prepr. **34/1**, 132 (1993);

- g) J. S. Moore, Polym. Prepr. 34/1, 170 (1993).
- [11] a) E. M. Graham, V. M. Miskowski, J. W. Perry, D. R. Coulter, A. E. Stiegman, W. P. Schaefer, R. E. Marsh, J. Am. Chem. Soc. 111, 8771 (1989);
  b) A. E. Stiegman, E. Graham, K. J. Perry, L. R. Khundkar, L. T. Cheng, J. W. Perry, J. Am. Chem. Soc. 113, 7658 (1991);
  c) N. Matsuzawa, D. A. Dixon, J. Phys. Chem. 96, 6232 (1992);
  d) L. T. Cheng, W. Tam, S. R. Marder, A. E. Stieg-

a) L. T. Cheng, W. Tam, S. K. Marder, A. E. Stiegman, G. Rikken, C. W. Spangler, J. Phys. Chem. **95**, 10643 (1991);

e) Y. Sugyama, Y. Suzuki, T. Nishama, T. Takesono, Jpn. Kokai Tokkyo Koho JP 05,100,263 [93,100,263] (1993).

- [12] J. Tsibouklis, J. P. Cresswell, N. Kalita, C. Pearson, P. J. Maddaford, H. Ancelin, J. Yarwood, M. J. Goodwin, N. Carr, W. J. Feast, M. C. Petty, J. Phys. D: Appl. Phys. 22, 1608 (1989).
- [13] T. J. Marks, M. A. Ratner, Angew. Chem., Int. Ed. Engl. 34, 155 (1995).
- [14] M. S. Wong, J. F. Nicoud, Tetrahedron Lett. 35, 6113 (1994).
- [15] A. Godt, J. M. F. Fréchet, J. E. Beecher, Macromol. Chem. Phys. **196**, 133 (1995).
- [16] a) J. Suffert, R. Ziessel, Tetrahedron Lett. 32, 757 (1991);

b) P. D. Beer, O. Kocian, R. J. Mortimer, C. Ridgway, J. Chem. Soc., Chem. Commun. 1460 (1991);
c) P. D. Beer, O. Kocian, R. J. Mortimer, C. Ridgway, J. Chem. Soc., Dalton Trans. 2629 (1993);
d) F. Vögtle, M. Frank, M. Nieger, P. Belser, A. von Zelewsky, V. Balzani, F. Barigelletti, L. De Cola, L. Flamigni, Angew. Chem., Int. Ed. Engl. 32, 1643 (1993);

e) F. M. Romero, R. Ziessel, Tetrahedron Lett. **35**, 9203 (1994);

f) A. C. Benniston, V. Grosshenny, A. Harriman, R. Ziessel, Angew. Chem., Int. Ed. Engl. **33**, 1884 (1994);

g) D. Tzalis, Y. Tor, Tetrahedron Lett. **36**, 6017 (1995).

[17] a) K. Kondo, S. Yasuda, T. Sakaguchi, M. Miya, J. Chem. Soc., Chem. Commun. 55 (1995);
b) B. König, H. Zieg, P. Bubenitschek, P. G. Jones, Chem. Ber. **127**, 1811 (1994).

[18] a) M. Rosenblum, N. Brawn, J. Papenmeier, M. Applebaum, J. Organomet. Chem. 6, 173 (1966);
b) J. Polin, H. Schottenberger, B. Anderson, S. F. Martin, Org. Synth. 73, 262 (1995).

- [19] a) M. D. Rausch, A. Siegel, L. P. Klemann, J. Org. Chem. 31, 2703 (1966);
  b) K. Schlögl, W. Steyrer, J. Organomet. Chem. 6, 399 (1966);
  c) M. D. Rausch, A. Siegel, J. Org. Chem. 34, 1974 (1969).
- [20] M. Wildschek, C. Rieker, P. Jaitner, H. Schottenberger, K. E. Schwarzhans, J. Organomet. Chem. **396**, 355 (1990).
- [21] J. L. Long, Angew. Chem., Int. Ed. Engl. 34, 21 (1995).
- [22] J. W. Perry, A. E. Stiegman, S. R. Marder, D. R. Coulter (R. A. Hann, D. Bloor (eds.);
  in: Organic Materials for Nonlinear Optics), Spec. Publ., Royal Soc. Chem. 69, 189 (1989).
- [23] a) H. Nock, H. Schottenberger, J. Org. Chem. 58, 7045 (1993);
  b) C. Bubeck, A. Baumann, private communication (1993).
- [24] M. Rosenblum, N. M. Brawn, D. Ciappenelli, J. Tencrede, J. Organomet. Chem. 24, 469 (1970).
- [25] A. Kasahara, T. Izumi, M. Maemura, Bull. Chem. Soc. Jpn. 50, 1021 (1977).
- [26] M. Sato, E. Mogi, Organometallics 14, 3157 (1995).
- [27] a) T. Imamoto, T. Kusumoto, Y. Tawarayama, Y. Sugiura, T. Mita, Y. Hatanaka, M. Yokoyama, J. Org. Chem. 49, 3904 (1984);
  b) M. Suzuki, Y. Kimura, S. Terashima, Chem. Lett. 1543 (1984).
- [28] F. Waugh, D. R. M. Walton, J. Organomet. Chem. 39, 275 (1972).
- [29] a) K. M. Park, G. B. Schuster, J. Org. Chem. 57, 2502 (1992);
  b) H. J. Bestmann, H. Behl, M. Bremer, Angew. Chem., Int. Ed. Engl. 28, 1219 (1989).
- [30] F. R. Lemke, D. J. Szalda, R. M. Bullock, J. Am. Chem. Soc. 113, 8466 (1991).
- [31] C. Lambert, S. Stadler, G. Bourhill, C. Bräuchle, Angew. Chem., Int. Ed. Engl. 35, 644 (1996).
- [32] H. Schottenberger, M. Buchmeiser, J. Polin, K. E. Schwarzhans, Z. Naturforsch. 48 b, 1524 (1993).
- [33] G. Wittig, P. Raff, Liebigs Ann. Chem. 573, 195 (1951).