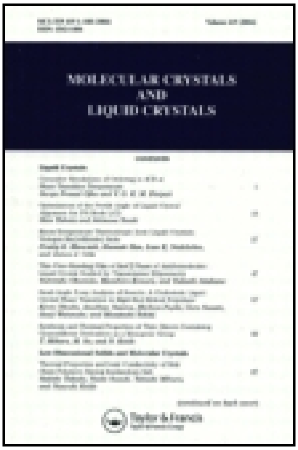

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Oligo(ethynylene-p-phenylen)ic and Benzilic Spacers for the Modular Construction of Organometallic NLO-Phores

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Oligo(ethynylene-*p*-phenylen)ic and Benzilic Spacers for the Modular Construction of Organometallic NLO-Phores

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The preparation and characterization of oligo(ethynylene-*p*-phenylene)s, $R-(C\equiv C-p-C_6H_4-)_nR'(C_{8n}H_{4n}RR'\ n=2\text{–}4)$ **1–13**, and 4,4′-diethynylbenzils, $R-C\equiv C-(p-C_6H_4)\text{–}CO-CO-(p-C_6H_4-)C\equiv C-R'$ **14–18** is reported. An economic strategy from easily accessible precursors towards extended 1,4-phenyleneacetylenes is presented with the synthetic sequence essentially based on repeated Pd/Cu-catalyzed Hagihara coupling of haloarenes with terminal ethynes. The linear and rigid hydrocarbon modules **2, 4, 6, 7** and 4,4′-diethynylbenzil have been chosen as spacers with inherent synthetic potential and satisfy equal structural confinements in principle. Functionalization with metallocenes, particularly ferrocene **14–18** and ruthenocene **11, 12, 18** and with ethynyltriphenyl borate **13** yields molecular structures with distinctive advantages for the field of nonlinear optics. Monosubstituted derivatives have been prepared as well as homo-and heteronuclear bimetallic species. Anionic rigid rod representatives supplement preceding cationic cobaltocenium derivatives. The salt character of the latter materials appears strikingly favorable to molecular solids with controllable aggregation.

Numerical assessment corresponds to the following compounds: bis(2-hydroxy-2-methylethyl)-$C_{18}H_8$-ethynylene-*p*-phenylene (**1**); $C_{18}H_{10}$-ethynylene-*p*-phenylene (**2**); bis(2-hydroxy-2-methylethyl) $C_{26}H_{12}$-ethynylene-*p*-phenylene (**3**); $C_{26}H_{14}$-ethynylene-*p*-phenylene (**4**); bis (2-hydroxy-2-methylethyl) $C_{34}H_{16}$-ethynylene-*p*-phenylene(**5**); $C_{34}H_{18}$-ethynylene-*p*-phenylene (**6**); 1, 4-bis ($C_{16}H_9$-ethynylene-*p*-phenylene) butadiyne(**7**); ($C_{18}H_9$-ethynylene-*p*-pheny-lene) trimethylsilane (**8**); ($C_{18}H_9$-ethynylene-*p*-phenylene)carboxaldehyde (**9**); ($C_{18}H_8$-ethynylene-*p*-

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phenylene) dicarboxaldehyde (**10**); ($C_{18}H_9$-ethynylene-*p*-phenylene) ruthenocene (**11**); ($C_{18}H_8$-ethynylene-*p*-phenylene)biruthenocene (**12**); potassium ($C_{18}H_9$-ethynylene-*p*-phenylene) triphenyl borate (**13**) 4-(ferrocenylethynyl)-4′-bromobenzil (**14**); 4-(ferrocenylethynyl)-4′-(3-hydroxy-3-methyl-but-1-ynyl)benzil (**15**); 4-(ferrocenylethynyl)-4′-(trimethylsilylethynyl)benzil (**16**); 4, 4′-bis(ferrocenylethynyl)benzil (**17**); 4-(ferrocenylethynyl)-4′-(ruthenocenylethynyl)benzil (**18**).

Keywords: Tolan; metallocene; nonlinear optics

INTRODUCTION

Current investigations on extended π-conjugated systems are particularly stimulated by the outstanding mechanical properties of polymers and composites, as well as by the potential of electro-and photoactive matrices and by the innovative impulses of molecular electronics and photonics. Among the huge number of appropriate systems, oligo(ethynylene-*p*-phenylene)s [1], R—($C{\equiv}C$-*p*-C_6H_4—)$_n$R′, attract exceptional attention. Polymers and copolymers result in networks with long-term orientational stability and rigid-rod reinforced thermosets with favorable high performance/high temperature characteristics. Tolan-based mesogens [2], functional diphenylacetylenes [3] and diphenylacetylene end-capped polyimides [4] result from application-oriented materials design. Oligomers enable well-defined molecular structures with pronounced linearity and rigidity, thus stimulating the construction of molecular wires [5], which results in one of the most exciting challenges in synthesis. The conformational invariability of elongated (ethynylene-*p*-phenylene)s will be advantageous to overcome the restrictions and limitations of nanolithographic methods in forthcoming applications. Proper functionalization results in self-assembled monolayers with potential in the manufacture of molecular electronic devices [6] and in exceptionally stable $\chi^{(3)}$ nonlinear optical materials with expected high hyperpolarizabilities [7]. Organized superlattices of organic ionomers offer a promising alternative to poled polymers and LB films in the construction of NLO materials [8].

In this article we report the stepwise elongation of (ethynylene-*p*-phenylene)s as well as the functionalization of 4, 4′ -diethynyltolan and 4, 4′-diethynylbenzil. The mono— and α,ω-disubstituted materials were selected on the basis of their potential as low-cost building blocks for the field of nonlinear optics.

HOMOLOGOUS (ETHYNYLENPHENYLENE)S AND BENZILIC SPACERS

Several synthetic strategies towards poly(ethynylenephenylene)s are known.The parent compound tolan [9] and corresponding oligomers [10] have initially been prepared from stilbene derivatives in an addition-elimination reaction, i.e. by bromination and subsequent alkaline dehydrobromination. Recently, the Pd-mediated coupling of halobenzenes with terminal ethynes according to Sonogashira and Hagihara [11] has prevailingly been adopted as a selective step-by-step approach and method of choice. The application of alternative methods [12] is conspicuously scarce.

Oligo(ethynylene-*o*-phenylene)s [13] have been prepared as pure hydrocarbon precursors to one-dimensional conducting graphite-like strands, as π-electron donors that can be used in D/A complexes and as hyperpolarizable donar-acceptor α, ω-disubstituted chromophores with application in nonlinear optics. The mild reaction conditions have even been proved to be compatible with prefunctionalized modules towards paramagnetic oligo(ethylene-*m*-phenylene)s [14] with antiferromagnetic coupling. The rational construction of phenylacetylene based dendrimers and molecular crystals [15] almost exclusively made of oligo(ethynylene-*m*-phenylene) skeletons utilizes 5-substituted (3,3-diethyltriazene-1-yl)-3-trimethylsilylethynylbenzenes and similar precursors. *t*-Butyl substituents at the 5-position serve as solubility mediators. Ethyne deprotection and again the Pd-catalyzed cross-coupling with halobenzenes turned out to be the most effective strategy towards these types of phenylacetylene based macromolecules.

The major problem in the elongation of rod-like poly(phenyleneacetylenes) arises from their very poor solubility with an increase of chain length which becomes particularly pronounced with oligo (ethynylene-*p*-phenylene)s [5b, 7a, 16]. Since conjugated oligomers for individual nonlinear optics applications require the processability into films or fibers, properties like insolubility and infusibility of unyielding macromolecules require solutions. To make sheer hydrocarbons more soluble, 2,5-dialkyl-*p*-phenylenes [5b], 2,5-dialkoxy-*p*-phenylenes [16] or *N*,*N*,*N*′,*N*′-tetraalkyl-2,5-phenylenediamines [17] with different types of side chains have been used and resulted very recently in remarkable polymers with 24 and 40 repeating units [16b] on average and in well-defined oligomers with 15 alternating ethynylene-*p*-phenylene units [5b]. The preparation of appropriate starting materials in these syntheses, however, demands additional effort. An approach to oligo(ethynylene-*p*-phenylene)s that succeeds without imposed substituents has previously been reported [7a]. However, a more convenient and inexpensive procedure from readily available precursors was called for. The aim was to develop a strategy which is distinguished by the ease of accessibility of educts and products, comprising suitable procedures, and high over-all efficiency. The compilation of plain building blocks relentlessly abuts on solubility limitations and certainly allows medium-mass oligo (ethynylene-*p*-phenylene)s only. This may be reputed as a drawback.

It seems that the maximum length of corresponding calamitic chromophores that can be further funcionalized by the methods issued has already been reached with $C_{34}H_{18}$-ethynylene-*p*-phenylene **6**.

4,4′-Diethynylbenzil has been chosen as an alternative spacer complementary to 4,4′-diethynyltolan which basically satisfies the same confinements required by $\chi^{(3)}$ NLO-phores. Credit is done to this bridging ligand by the conceivable convertability of this type of spacer into nondegenerate conducting stilbene derivatives [18] by reduction into the corresponding diphenylglycol and subsequent Corey-Winter olefin synthesis or via the corresponding dianion which reacts as nucleophile with dimethyl sulfate and acetyl chloride as well as into tolan derivatives via dihydrazones and subsequent nitrogen elimination or by conversion of the diketone in the presence of Ti(0)diaryls [19]. None the less, the most striking structural attribute that distinguishes benzils from tolans is their internal flexibility which increases solubility. While the α, ω-coupling of 4,4′-dibromobenzil with monosubstituted 4,4′-diethynyltolans or even 4,4′-diethynylbenzils and conversion towards accurately configured molecular structures is very inviting, it has not yet been tried by keenly underlines the synthetic potential of the modular construction principle.

α,ω-FUNCTIONALIZATION OF 4,4′-DIETHYNYLTOLAN AND 4,4′-DIETHYNYLBENZIL

Although the progress in the synthesis of poly(ethynylenephenylene)s and corresponding copolymers [16] is quite satsifactory, the attempts to functionalize adequate oligomers made-to-measure are remarkably scarce. Apart from lateral substituents [5a, b, 15–17] which counteract insolubility and in exceptional cases induce mesophases [15b, 16b], terminal functionalization is restricted to α,ω-substituted *ortho*-phenyleneacetylenic NLO-phores [13c] which apply dimethylaniline donor and nitrobenzene acceptor groups, and *meta*-phenyleneethynylenes [14], with pendent nitronyl nitroxide radicals to gain high spin concentrations, targeted on the realization of organic ferromagnets. The usefulness of (ferrocenyl $C_{18}H_8$-ethynylene-*p*-phenylene)thiophenol, phenylenemethylsulfide, —methyl sulfoxide and —methylsulfone derivatives in the construction of self-assembled monolayers that can be chemisorbed on metal surfaces has recently been proposed [6].

Basic requirments for NLO-phores with potential for the fabrication of $\chi^{(3)}$ nonlinear optical devices are high nonlinear optical susceptibilities, high laser damage threshold, improved optical transparency and improved processability if seen in the context of polymers, as well as noncentrosymmetric molecules and matrices for $\chi^{(2)}$ NLO systems. Application of organic salts affords the opportunity of constitutional tailoring of second-order nonlinear optical materials by ion metathesis [8b, 20]. The functionalization of 4,4′-diethynyltolan with donor substituents like ferrocene, inductive acceptor substituents like perfluoroarenes [7a] or cyclobut-3-en-1,2-diones [7b], and cobaltocenium species [7a] aims at extended conjugated systems to accomplish large and ultrafast optical nonlinearities. Monosubstituted derivatives have been prepared as well as homo- and heteronuclear bimetallic species. In this paper, ruthenocene is presented as an additional donor metallocene and ethynyltriphenyl borate as the anionic counterpart to cobaltocenium derivatives. Trimethylsilyl and 3-hydroxy-3-methylbutyn-1-yl groups have prevailingly been used as protecting groups for terminal acetylenes [21]. The salt character of ethynyltriphenyl borate and cobaltocenium based NLO-phores appears strikingly favorable for molecular solids with controllable architecture. The synthesis of this novel series of compounds is discussed in the following.

RESULTS AND DISCUSSION

$C_{8n+2}H_{4n+2}$-Ethynylene-*p*-phenylenes. Ethynylene-2, 5-thiophenylene and ethynylene-*p*-phenylene oligomers are among the most promising systems for molecular wires [5b, 22]. Laterally branched derivatives of remarkable length have already been presented. With regard to stability, the latter family of chromophores appears favorable and encouraged the development of an easy step-by-step approach to genuine rigid-rod oligomers. The progenitor of the $C_{8n+2}H_{4n+2}$-ethynylene-*p*-phenylene series $C_{10}H_6$-ethynylene-*p*-phenylene (4,4′-diethynylbenzene; $n = 1$) has been reported quite early; however, corresponding preparation methods in general suffer from severe insufficiencies [23]. Up to now the most effective and quite reasonable method towards 1,4-diethynylbenzene is based on the Hagihara coupling and applies 1,4-diiodobenzene and trimethylsilylacetylene [24]. Subsequent alkaline hydrolysis of the stable TMS-protected intermediate under quite mild conditions affords 1,4-diethynylbenzene, which is prone to polymerization.

Theoretical studies on optimized NLO-phores indicted two important results in principle: The hyperpolarizability density ρ ($\rho = \beta_{\mathrm{vec}}$/molecular volume) of polyenes and polyphenylenes passes a maximum value with increased chain length at $n = 4$ and $n = 20$ respectively [25]. In addition, β_{vec} for α, ω-diphenylpolyene derivatives increases for $n = 2, 3, 4$, whereas β_{vec} in α,ω-diphenylpolyynes remains almost unbiased by an increased number of internal ethyne units. From these results, $C_{18}H_{10}$-ethynylene-*p*-phenylene **2** (4,4′-diethynyltolan; $n = 2$) may be considered as an exquisite spacer of accurate length in materials for nonlinear optics. Apart from these considerations and in contrast to 1,4-diethynylbenzene, the compound represents a remarkable stable chromophore. The accessibility by different strategies [7a] proves to be an additional bonus. However, a new strategy had to be developed to make this starting material a quasi-bulk chemical. Pd(II)/Cu(I) catalyzed cross-coupling of 4,4′-dibromotolan [26], which is easily accessible in large quantities from 1,2-diphenylethane without particular experimental means, with the partially protected acetylene 2-methyl-3-butyn-2-ol, which is much cheaper than trimethylsilylacetylene, and subsequent double-sided deprotection with NaOH/toluene or potassium *tert.*-butanolate/THF turned out to be the method of choice. The smooth isolation of both the intermediate glycol **1** and 4,4′-diethynyltolan **2** after deprotection by filtration and recrystallization from acetonitrile makes this synthetic approach decidedly more preferable.

The conceptual lengthening of $C_{18}H_{10}$-ethynylene-*p*-phenylene is based on the α,ω-elongation of $C_{10}H_6$-ethynylene-*p*-phenylene. This approach necessitates a 4-halophenylacetylene synthon with a protected ethyne function. Accordingly, 4-iodoaniline has been converted into 4-(4-iodophenyl)-2-methyl-3-butyn-2-ol [27] which actually represents a valuable C_8H_4-synthon. Reaction of 2 meq with $C_{10}H_6$-ethynylene-*p*-phenylene under Hagihara conditions and subsequent hydrolysis of intermediate **3** yields $C_{26}H_{14}$-ethynylene-*p*-phenylene **4**(4-[4-ethynylphenylethynyl]-4′-ethynyltolan; $n = 3$) [28] . The product crystallizes from the filtered hot solution.

Essentially the same procedure via glycol **5** yields $C_{34}H_{18}$-ethynylene-*p*-phenylene **6** (4,4′-bis(ethynylphenylethynyl)tolan; $n = 4$) from 4-(4-iodophenyl)-2-methyl-3-butyn-2-ol and $C_{18}H_{10}$-ethynylene-*p*-phenylene **2**. Utilization of 2.4 meq of the 4-iodophenylacetylene synthon guarantees double-sided ethynylation. The pure product was isolated from THF extracts by Soxhlet extraction.

Owing to solubility problems $C_{8n+2}H_{4n+2}$-ethynylene-*p*-phenylenes with $n > 4$ are hardly tangible from continued sequenzing. However, prospective alternatives are the elongation of [4-halo($C_{8n}H_{4n}$)]-2-hydroxy-2-methylethyl synthons ($n > 1$), which have yet not reached their solubility limitations, and Pd-mediated coupling with $C_{8n+2}H_{4n+2}$-ethynylene-*p*-phenylenes ($n = 2$(**2**), 3(**4**), 4(**6**)) as well as oxidative dimerization of terminal acetylenes [29]. Dimerization of $C_{18}H_{10}$-ethynylene-*p*-phenylene **2** to 1,4-bis($C_{16}H_9$-ethynylene-*p*-phenylene)butadiyne **7** under Glaser conditions proceeded smoothly without formation of undesired oligomers owing to the very low solubility of the coupling product. The corresponding preparation of 1,4-bis($C_{32}H_{17}$-

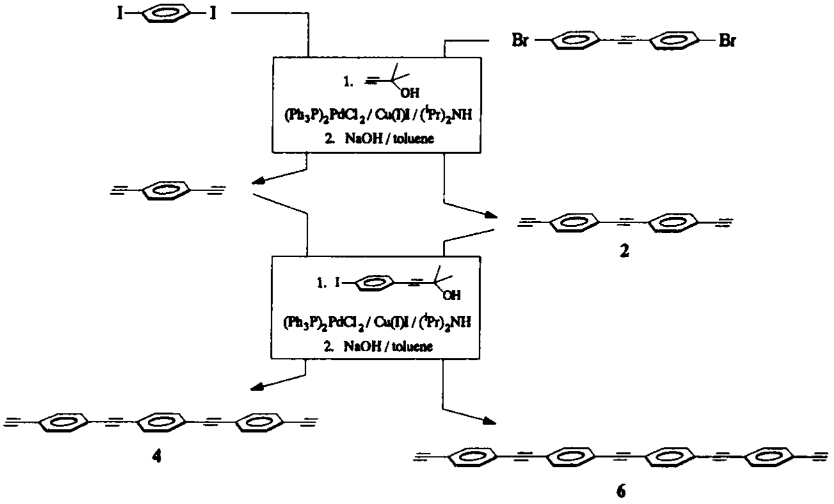

FIGURE 1 Synthesis of $C_{8n+2}H_{n+2}$-ethynylene-*p*-phenylenes.

ethynylene-*p*-phenylene)butadiyne by dimerization of $C_{34}H_{18}$-ethynylene *p*-phenylene **4** would have resulted in a 64 Å spacer. However, despite of promising analytical data it was not possible to obtain the complete set for this chromophore which therefore must be regarded as a postulate.

Substituted $C_{8n+2}H_{4n+1}$-Ethynylene-*p*-phenylenes. Basic considerations in the design of $\chi^{(3)}$ NLO-phores and the convenience of accessibility prompted to the functionalization of 1,4-diethynyltolan **2**. Monosubstituted products serve almost exclusively as precursors in the manufacture of heterofunctionalized $C_{8n}H_{4n}$-ethynylene-*p*-phenylenes. Occasionally these materials resulted as by-products from incomplete conversion towards symmetrically disubstituted $C_{8n+2}H_{4n}$-ethynylene-*p*-phenylenes but are accessible from a stoichiometric 1:1 cross-coupling in principle. Since the proposed step-by-step approach via

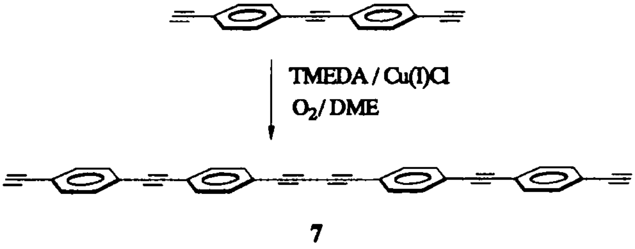

FIGURE 2 Dimerization of ethynylene-*p*-phenylenes.

modules is of broad applicability, ethynylbenzil intermediates have been used exactly in the same way as the corresponding diethynyltolans. This displays the flexibility of the underlying concept towards molecular finalities.

Trimethylsilyl monoprotection of 4,4′-diethynyltolan **2** with trimethylchlorosilane yields ($C_{18}H_9$-ethynylene-*p*-phenylene)trimethylsilane **8** (4-(2-trimethylsilylethnyl)-4′-ethynyltolan) in very good yields. However, the product which has not been used in subsequent reactions has hardly been characterized. Formylation using *N*,*N*-dimethylformamide lead to ($C_{18}H_9$-ethynylene-*p*-phenylene carboxaldehyde **9** (4-(2-formylethynyl)-4′-ethynyltolan) as a byproduct in the synthesis of the corresponding dialdehyde **10**. The syntheses of ($C_{18}H_8$-ethynylene-*p*-phenylene)ferrocene [6a, 7a], (ferrocenyl-$C_{18}H_8$-ethynylene-*p*-phenylene)cobaltocenium hexafluorophosphate [7a], (ferrocenyl-$C_{18}H_{18}$-ethynylene-*p*-phenylene)pentafluorobenzene [7a] and 4-(ferrocenyl-$C_{18}H_8$-ethynylene-*p*-phenylene)thiophenol [6a] and its methylsulfide, methyl sulfoxide and methyl sulfone derivatives have already been discussed. ($C_{18}H_9$-Ethynylene-*p*-phenylene)ruthenocene **11** has been prepared from **2** by coupling with the cuproruthenocene dimethylsulfide complex [30] in an inversely conducted Stephens-Castro reaction by analogy with the initially reported synthesis of ($C_{18}H_9$-ethynylene-*p*-phenylene)ferrocene [7a]. Direct ethynylation of triphenylboran [31] via the monolithium acetylide of **2** yielded the anionic detergens potassium ($C_{18}H_9$-ethynylene-*p*-phenylene)-triphenyl borate **13** which is the only covalently bonded organic anion in rigid NLO-oligomers so far [32]. Comparable systems that contribute to the promising class of ionic NLO-phores are cognate cobaltocenium derivatives [7a], 4-(2-ferrocenylvinylene)-*N*-alkylpyridinium [33], 4-[-2-(*p*-pheny-lenevinylene)]-*N*-alkylpyridinium as well as 4-(*p*-phenyleneethynylene)-*N*-alkylpyridinium salts [34]. Solid state studies of organic ionomers of that kind obviously emerge as challenging frontiers.

Disubstituted $C_{8n+2}H_{4n+1}$-Ethynylene-*p*-phenylenes. α, ω-Functionalization of 4,4′-diethynyltolan results in homo- and heterodisubstituted chromophores depending on the underlying objective. Formylation as described above via the dilithium acetylide of **2** leads to ($C_{18}H_8$-ethynylene-*p*-phenylene)dicarboxaldehyde **10** (4,4′-bis(2-formylethynyl)tolan. Compound **9** resulted as a byproduct. Transmetallation of metallocene-1-yl intermediates and coupling with *in situ* generated iodoacetylenes has been applied in the syntheses of ($C_{18}H_8$-ethynylene-*p*-phenylene) biferrocene [7a] and ($C_{18}H_8$-ethynylene-*p*-phenylene) biruthenocene **12** (4, 4′-bis(ruthenocenylethynyl)tolan). Even here the formation of the corresponding monometallocenyl $C_{18}H_9$ derivative (compound **11** in the case of ruthenocene) has been ascertained. Transmetallation on the acetylide site in contrary proved favorable in the coupling with

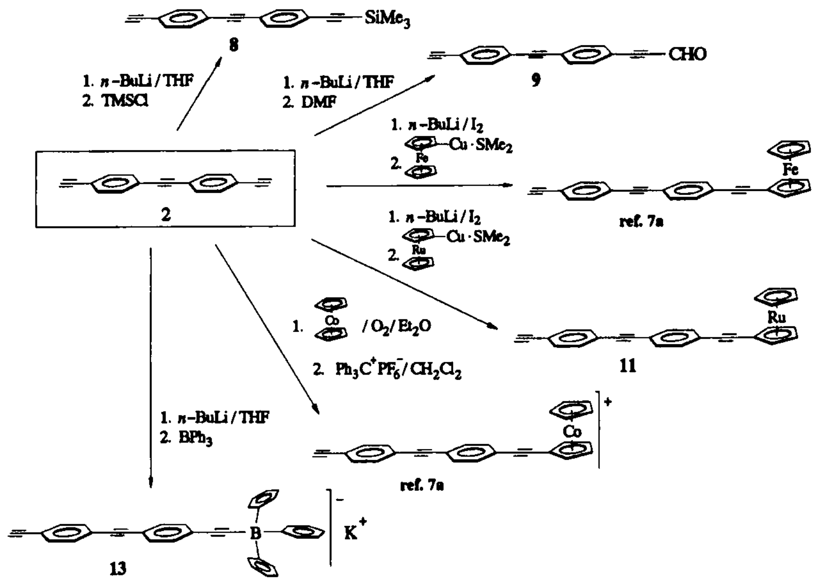

FIGURE 3 Synthesis of $C_{18}H_9$-ethynylene-p-phenylenes by direct ethynylation and inverse Stephens-Castro reactions.

squaric acide chloride and yielded 3-ferrocenyl-4-(ferrocenyl-$C_{18}H_8$-ethynylene-p-phenylene)cyclobut-3-en-1,2-dione [7b]. Two different strategies to cobaltocene based structures, particularly ($C_{18}H_9$-ethynylene-p-phenylene)cobaltocenium hexafluorophosphate, ($C_{18}H_8$-ethynylene-p-phenylene) bicobaltocenium dihexafluorophosphate and (ferrocenyl-$C_{18}H_8$-ethynylene-p-phenylene)cobaltocenium hexafluorophosphate, have already been proposed [7a]. The Hagihara coupling of ($C_{18}H_9$-ethynylene-p-phenylene)ferrocene [6a, 7a] with appropriate haloarene precursors lead to the pentafluorobenzene [7a] and thiophenol, methyl sulfide, methyl sulfoxide and methyl sulfone derivatives [6a] as described above. The same strategy but different types of precursors yielded ferrocenyl($C_{18}H_8$-ethynylene-p-phenylene)trimethylsilane [6a]. The target compound potassium ferrocenyl($C_{18}H_8$-ethynylene-p-phenylene)triphenyl borate, which should be accessible from direct ethynylation according to compound **13** and potassium(ferrocenylethynylene)triphenylborate [35], could not be clearly characterized.

Functionalization of Benzil Derivatives. The preparation of benzil derivatives follows essentially the same scheme as described for tolan based materials. The incorporation of functionalities via ethynes has been applied to the syntheses of ferrocene derivatives and it appears near at hand that akin derivatizations as described above will be effective as well. The homodinuclear complexe 4,4′-

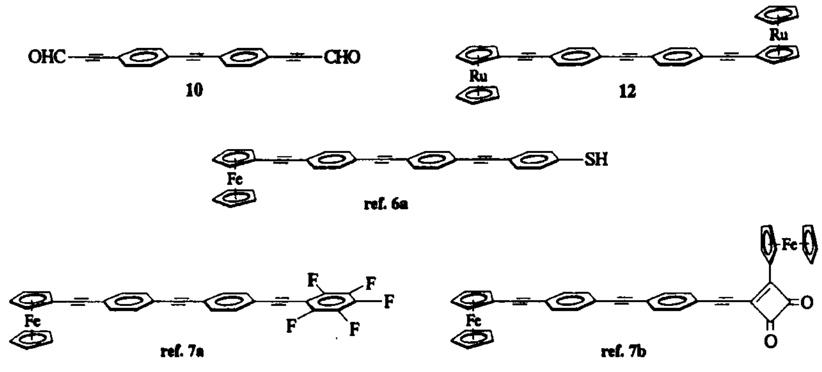

FIGURE 4 α, ω-Disubstituted $C_{18}H_8$-ethynylene-*p*-phenylenes.

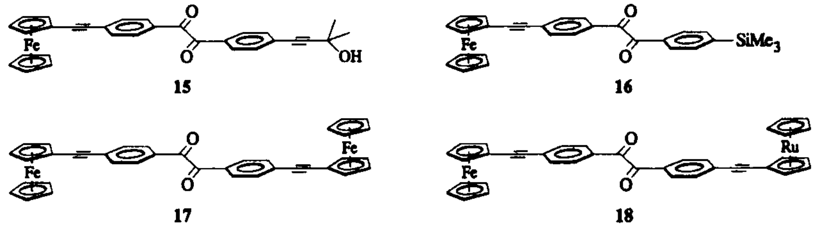

FIGURE 5 Homo- and heteronuclear 4, 4′-diethynylbenzil derivatives.

bis(ferrocenylethynyl)benzil **17** has been prepared by Pd/Cu catalyzed coupling of 4, 4′-dibromobenzil and ethynylferrocene [36]. The corresponding monosubstituted 4-(ferrocenylethynyl)-4′-bromobenzil **14**, a byproduct in the synthesis of **17**, serves as precursor to 4-(ferrocenylethynyl)-4′-(3-hydroxy-3-methylbut-1-ynyl)benzil **15** and 4-(ferrocenylethynyl)-4′-(trimethylsilylethynyl)benzil **16**. These systems may be easily converted into bifunctional systems after deprotection or even be elongated by dimerization as described for ethynylene-*p*-phenylenes. Ethynylruthenocene [30] and precursor **14** finally yielded the heterodinuclear Fe/Ru system 4-(ferrocenylethnyl)-4′-(ruthenocenylethynyl)benzil **18**. Both flexibility and aptidude of the modular approach towards various functionalized ethynylene-*p*-phenylenes are even guaranteed for benzil derivatives without limitations.

EXPERIMENTAL SECTION

General Details. All experiments were carried out under an inert atmosphere using standard Schlenk technique unless otherwise indicated. Reagent grade *n*-hexane, diethyl ether, THF, DME, toluene and benzene were distilled under argon from sodium benzophenone ketyl 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 Gel for column chromatography was purchased from Fluka. The analytical equipment for spectroscopic characterization comprises: Bruker AM 300 and AM 200 (^{1}H-NMR, ^{13}C-NMR; δ [ppm] *vs.* TMS; 25°C), several quaternary ^{13}C-NMR peaks are missing because of low solubilities; FTS-40 BIORAD and Nicolet 510M FT-IR (IR; ν [cm^{-1}]); CH-7 MAT (EI, 70 eV) and Finnigan MAT 90 (MS). Mass spectroscopy of ionic derivatives was performed at the Technische Universität München and elemental analysis by the Mikroanalytisches Laboratorium, Physikalisches Institut der Universität Wien.

4,4'-Dibromotolan [26]. Modifications resulted in the following synthesis: Diphenylethane (5.0 g, 27 mmol) is dissolved in glacial acetic acid (55 mL). After the addition of water (2.7 mL), bromine (6.83 mL) is added via syringe and the reaction mixture is heated under reflux for 2 h. The hot solution is filtered through a glass frit (G3) and the remaining crude product 4,4'-α,β-tetrabromo-α,β-diphenylethane (5.8 g, 43%) subsequently washed with small portions of glacial acetic acid and ether.

Potassium *tert*-butanolate (9.8g) is dissolved in THF (150 mL) in a separate flask, the intermediate tetrabromodiphenylethane (3.5 g) is added and the mixture refluxed for 45 min. When cooled to ambient temperature the reaction mixture is filtered and the solvent is removed. The remaining crude product is taken up in dichloromethane, washed with water, dried and 4,4'-dibromotolan (3.75 g, 69%) recrystallized from dichloromethane.

α,ω-Bis(2-hydroxy-2-methylethyl)-$C_{18}H_8$-ethynylene-*p*-phenylene (4,4'-Bis(3-hydroxy-3-methylbutynyl)tolan) **(1)**. 4,4'-Dibromotolan (14.5 g, 43 mmol) and 2-methyl-3-butyn-2-ol(16.7 mL, 172 mmol) were dissolved in dry disopropylamine (500 mL). Catalytic amounts of $(Ph_3P)_2PdCl_2$ (0.60g, 0.86 mmol) and CuI (0.16g, 0.86 mmol) were added and the resulting suspension was refluxed under inert atmosphere for at least 72 hours. The hot mixture was then filtered by suction through a sintered glass frit (D3). After evaporation of the amine under reduced pressure, the residue was taken up in acetonitrile (50 mL), sonificated for a few minutes and again collected on a sintered glass frit (D3). The remaining material was finally washed with cold acetonitrile (3 × 50 mL) and dried in a rapid stream of air, yielding a filthy white product (11.0g, 32.2 mmol, 75%), which was pure enough to be used in the subsequent deprotection step. Further purification of **(1)** may be achieved by recrystallization from acetonitrile (9.13 g, 26.6 mmol, 62%). mp 211°C; ^{1}H-NMR ($CDCl_3$) 1.60 (s, 12 H, $C\underline{H}_3$), 2.00 (s, 2 H, $O\underline{H}$), 7.40

(m, 8 H, H_{aryl}); ^{13}C-NMR ($CDCl_3$) 31.38 ($\underline{C}H_3$), 65.70, 81.85, 90.80, 95.76, 122.85, 131.42, 131.58; IR(KBr) 3471 m, 2984 m, 2938 w, 2359 w, 2226 w, 1514 s, 1452 w, 1404 m, 1371 s, 1354 m, 1273 m, 1209 w, 1186 s, 1161 vs, 1105 m, 1018 w, 962 s, 928 w, 903 s, 791 m, 630 m, 567 s, 538 s, 470 m, 451 m; MS calcd for $C_{24}H_{22}O_2$ 342.44, MS found m/z 342($M^{+\cdot}$, 17%).

$C_{18}H_{10}$-Ethynylene-*p*-phenylene (4,4′-Diethynyltolan) [37] (**2**). A vigorously stirred mixture of 4,4′-bis(3-hydroxy-3-methylbutynyl)tolan (**1**) (6.10 g, 17.8 mmol) and NaOH pellets (14.4g, 356 mmol) in toluene (400 mL) was refluxed for 48 hours. When cooled down to room temperature, the suspension was filtered through a Büchner funnel, and the filtrate was evaporated under reduced pressure. Double recrystallization from acetonitrile yielded analytical pure 4,4′-diethynyltolan (**2**) (3.62 g, 16.0 mmol, 90%).

α, ω-Bis(2-hydroxy-2methylethyl)$C_{26}H_{12}$-ethynylene-*p*-phenylene (2-Hydroxy-2-[2′-hydroxypropyl-($C_{26}H_{12}$-ethynylene-*p*-phenylenediyl)]propane) (**3**). $(Ph_3P)_2PdCl_2$ (22 mg, 0.032 mmol) and CuI (6.1 mg, 0.032 mmol) were added to a carefully degassed solution of 1,4-diethynyl benzene [24] (0.20 g, 1.6 mmol) and 4-(4-iodophenyl)-2-methyl-3-butyn-2-ol [27] (0.92 g, 3.2 mmol) in dry diisopropylamine. The mixture was stirred for 24 hours at room temperature and then poured through a suction filter (D3). The filthy white product was successively washed with further 50 mL diisopropylamine and diethyl ether (150 mL) and dried in a rapid stream of air. The amorphous crude product was taken up in a saturated NH_4Cl-solution (200 mL) and the resulting suspension was warmed to about 65°C, stirred for 30 minutes and finally cooled down to room temperature. The water-insoluble product (**3**) was collected on a suction filter (D3), washed with saturated NH_4Cl-solution (50 mL), water (200mL) and EtOH (200 mL) and finally dried in the air (0.65g, 1.5 mmol, 92%). mp > 250°C; IR (KBr) 3463 m, 3039 m, 2984 m, 2936 m, 2226 w, 1921 w, 1676 w, 1516 s, 1451 w, 1408 m, 1371 s, 1356 s, 1312 w, 1273 s, 1180 m, 1161 s, 1105 s, 1016 w, 962 s, 928 w, 903 s, 839 vs, 791 m, 723 w, 661 w, 573 s, 563 s, 549 m, 540 s, 493 m, 439 m MS calcd for $C_{32}H_{26}O_2$ 442.56, MS found m/z 442 ($M^{+\cdot}$, 100%).

$C_{26}H_{14}$-Ethynylene-*p*-phenylene (4-[2-(4-Ethynlphenyl)ethynyl]-4′-ethynyltolan) (**4**). 2-hydroxy-2-[2′-hydroxypropyl-($C_{26}H_{12}$-ethynylene-*p*-phenylene)]propane (**3**) (0.50 g, 1.1 mmol) and NaOH pellets (2.2 g, 55 mmol) were suspended in toluene (200 mL) and refluxed for 24 hours under inert atmosphere. The hot mixture was filtered through a Büchner funnel and slowely cooled down to −20°C. After being stored at this temperature for 48 hours the resulting suspension of pure crystalline product was poured through an appropriate suction filter (D3). The residue (**4**) was finally washed with cold toluene and ether (25 mL of each) and dried on air (0.31 g, 0.95

mmol, 87%). mp 95°C (decomp.); ^{1}H-NMR ($CDCl_3$) 3.16 (s, 2 H, $C{\equiv}C\underline{H}$), 7.47 (m, 12 H, H_{aryl}); IR (KBr) 3434 m (traces of hydroxy-impurities), 3301 m, 3278 s, 1927 m, 1682 m, 1518 s, 1485 m, 1406 m, 1360 w, 1310 w, 1267 s, 1178 w, 1105 m, 1016 w, 837 s, 727 w, 692 m, 675 w, 667 m, 646 s, 625 s, 553 w, 542 vs, 507 w, 476 w, 438 m; CH-Anal. calcd for $C_{26}H_{14}$ C9546 s, 625 s, 553 w, 542 vs, 507 w, 476 w, 438 m; CH-Anal. calcd for $C_{26}H_{14}$ C 95.68, H 4.32, found C 95.22, H 4.53; MS calcd for $C_{26}H_{14}$ 326.40, MS found m/z 326 ($M^{+\cdot}$, 100%).

α, ω-Bis(2-hydroxy-2methylethyl)-$C_{34}H_{16}$-ethynylene-*p*-phenylene (2-Hydroxy-2-[2′-hydroxypropyl-($C_{34}H_{16}$-ethynylene-*p*-phenylene)]propane) (**5**). A solution of 4, 4′-diethynyltolan (2) (1.0 g, 4.4 mmol) and 4-(4-iodophenyl)-2-methyl-3-butyn-2-ol [27] (3.0g, 11mmol) in dry diisopropylamine (200 mL) was degassed carefully, combined with $(Ph_3P)_2PdCl_2$ (62 mg, 0.088 mmol) and CuI (16 mg, 0.088 mmol) and refluxed for 24 hours. After evaporation of the base under reduced pressure, the amorphous residue was taken up in a saturated NH_4Cl-solution (200 mL). The resulting suspension was warmed up to 65°C, stirred for 30 minutes at this temperature and then poured through a suction filter (D4). The crude product was washed successively with a saturated NH_4Cl-solution (50 mL), water (200 mL) and ice-cold ethanol (200 mL) and dried on air. Purification was achieved by extracting a homogeneous mixture of the filter sludge with an equivalent quantity of silica (silica G-60, 220–440 mesh) in an appropriate soxhlet apparatus, first with diethyl ether for 48 hours, then with THF for 120 hours. While the ether fraction may be discarded, the THF fraction was concentrated by evaporation of the solvent. The brownish residue was taken up in acetone (30 mL), suspended by sonification for 5 min, collected on a suction filter (D4), washed with further acetone until the filtrate was nearly colorless and (**5**) finally dried on air. mp > 250°C; IR (KBr) 3415 m, 3039 w, 2983 m, 2934 w, 2286 w, 1921 w, 1674 w, 1520 s, 1454 w, 1406 m, 1375 s, 1310 w, 1273 m, 1161 s, 1105 s, 1016 m, 962 s, 903 s, 839 vs, 793 m, 723 w, 584 m, 561 s, 536 s, 505 m, 480 m, 436 m; MS calcd for $C_{40}H_{30}O_2$ 542.68, MS found (FD, THF) m/z 542 ($M^{+\cdot}$, 14%).

$C_{34}H_{18}$-Ethynylene-*p*-phenylene (4,4′-Bis[2-(4-ethynlphenyl)ethynyl]tolan) (**6**). A suspension of 2-2-hydroxypropyl-$C_{34}H_{16}$-ethynylene-*p*-phenylene)]propane (5) (0.89 g, 1.4 mmol) and NaOH pellets (2.8 g, 70 mmol) in toluene (800 mL) was refluxed for 48 hours. The hot mixture was then filtered through a Büchner funnel, and the filtrate concentrated under reduced pressure. The red residue was taken up in ether (50 mL), sonificated for 3 minutes, collected on a suction filter (D4), washed with hexane (200 mL) and (**6**) dried on air (0.33 g, 0.77 mmol, 55%) mp > 230°C; IR (KBr)

3278 m, 1927 w, 1680 w, 1518 s, 1493 m, 1406 m, 1310 m, 1267 m, 1105 s, 1016 m, 839 vs, 727 w, 694 w, 665 w, 646 m, 625 s, 551 w, 540 s, 517 w, 478 w, 434 w; CH-Anal. calcd for $C_{34}H_{18}$ 95.75 C, 4.75 H, found 95.22 C, 4.60 H; MS calcd for $C_{34}H_{18}$ 426.52, MS found m/z 426 ($M^{+\cdot}$, 100%).

1,4-Bis($C_{16}H_9$-ethynylene-*p*-phenylenyl)butadiyne (**7**). A solution of 4,4′-diethynyltolan (**2**) (0.50 g, 2.2 mmol) in 20 mL of DME was added rapidly to a suspension of Cu(I)Cl (44 mg, 0.44 mmol) and TMEDA (87 mg, 0.75 mmol) in 20 mL DME. Air was passed through the mixture for 2 hours. After the solution was stirred at room temperature for 48 hours, it was filtered and the residue was washed with DME (200 mL) and diethyl ether (200 mL). The crude product was suspended in sat. aqueous NH_4Cl-solution (100 mL), warmed to 60–70°C and stirred for 30 minutes. The aqueous layer was filtered again, washed with an NH_4Cl-solution (50 mL), water (200 mL) and cold ethanol (100 mL) and (**7**) dried on air (0.29 g, 0.64 mmol, 58%) mp > 250°C; IR (KBr) 3278 m, 1925 w, 1601 m, 1499 s, 1404 s, 1267 s, 1105 s, 1016 m, 837 s, 690 w, 663 w, 644 m, 623 s, 542 s, 520 w, 451 w; CH-Anal. calcd for $C_{36}H_{18}$ C 95.98, H 4.02, found C 95.98, H 4.03; MS calcd for $C_{36}H_{18}$ 450.54, MS found m/z 450 ($M^{+\cdot}$, 28%).

($C_{18}H_9$-Ethynylene-*p*-phenylene)trimethylsilane (4-(2-Trimethylsilylethynyl)-4′-ethynyltolan) (**8**). A solution of 4,4′-diethynyltolan (**2**) (0.18 g, 0.8 mmol) in THF (50 mL) was cooled to −78°C and *n*-butyllithium (1.6 M in *n*-hexane, 0.50 mL, 0.8 mmol) was added with stirring under a stream of argon. The reaction mixture initially turned blue with subsequent formation of a voluminous precipitate. The system was brought to room temperature within 90 min, cooled again to −78°C and treated with trimethylchlorosilane (10 μL, 0.8 mmol) which resulted in the formation of a clear yellow solution. The reaction mixture was concentrated at a HV pump and the remaining residue purified by column chromatography under argon (Celit/Silica G-60741 5:1, 2 × 15 cm, *n*-pentane). The eluent was removed again and the residual white product (**8**) dried at the HV pump (0.25 g, 0.8 mmol), 100%) IR (KBr) 2160 ($C{\equiv}C$).

($C_{18}H_9$-Ethynylene-*p*-phenylene)carboxaldehyde (4-(2-Formylethynyl)-4′-ethynyltolan) (**9**) and **($C_{18}H_9$-Ethynylene-*p*-phenylene)dicarboxaldehyde** (4,4′-Bis(2-formylethynyl)tolan) (**10**). *n*-Butyllithium (2.5 M in hexane, 3.9 mL. 9.7 mmol) was added dropwise to a carefully degassed solution of 4,4′-diethynyltolan (**2**) (1.0 g, 4.4. mmol) in dry THF (120 mL) at −20°C. After 1.5 hours of stirring under inert atmosphere, the resulting suspension was cooled to −70°C and combined with dry DMF (0.81 g, 11 mmol). The cooling bath was removed and the temperature allowed to rise to room temperature. Stirring was continued for additional 45 min and occasional sonification

(Sonorex Bandulin) proved to raise the overall yields markedly. Subsequently, the mixture was poured into a vigorously stirred solution of 36% aqueous HCl (2.0 g) in ice-water (120 mL), neutralized by the addition of $NaHCO_3$, and extracted with Et_2O (3 x 100 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and finally chromatographed (Silica G-60, 220–440 mesh, 4 x 40 cm, hexane: diethyl ether 50:50) to give 4-(2-formylethynyl)-4′-ethynyltolan (**9**) (0.24 g, 0.94 mmol, 21%) as the first and 4,4′-bis(2-formylethynyl)tolan (**10**). (0.68 g, 2.4 mmol, 54%) as the second fraction. Both compounds were purified by recrystallization from CH_3CN. 4-(2-Formylethynyl-4′-ethynyltolan (**9**): mp 166°C; ^1H-NMR ($CDCl_3$) 3.17 (s, 1H), 7.51(m, 8H), 9.40 (s, 1H); ^{13}C-NMR ($CDCl_3$) 79.3, 83.1, 89.6, 90.3, 92.3, 94.2, 119.1, 122.5, 122.9, 126.0, 131.5, 131.7, 132.1, 133.1, 176.5; IR (KBr) 3246 s, 2962 s, 2242 m, 2185 s, 1660 vs, 1596 m, 1512 m, 1404 w, 1388 m, 1262 m, 1103 m, 1015 m, 982 m,828 m, 724 w, 701 w, 540 w, 451 w; MS calcd for $C_{19}H_{10}O$ 254.07, MS found m/z 254 ($M^{+\cdot}$, 100%). 4,4′-Bis(2-formylethynyl)tolan (**10**): mp 183°C (decomp.); ^1H-NMR ($CDCl_3$) 7.53 (m, 8H), 9.41 (s, 2H); ^{13}C-NMR ($CDCl_3$) 89.7, 91.9, 94.0, 119.6, 125.7, 131.9, 135.2, 176.5; IR (KBr) 3041 m, 2893 m, 2241 m, 2189 s, 1705 w, 1650 s, 1601 s, 1513 m, 1404 w, 1385 m, 1262 m, 1175 w, 1105 w, 1013 w, 981 s, 835 s, 821 s,728 m, 514 m, 449 w; MS calcd for $C_{20}H_{10}O_2$ 282.07, MS found m/z 282 ($M^{+\cdot}$, 100%).

($C_{18}H_9$-Ethynylene-*p*-phenylene)ruthenocene (4-(Ruthenocenylethynyl)-4′-ethynyltolan) (**11**) and **($C_{18}H_9$-Ethynylene-*p*-phenylene)biruthenocene** (4,4′-Bis(ruthenocenylethynyl)tolan) (**12**). a) Cuproruthenocene [30]: Ruthenocene (590 mg, 2.55 mmol) was dissolved in 20 mL of THF, the solution was cooled to −20°C and *t*-butyllithium (1.7 M in hexane, 1.5 mL, 2.55 mmol) was added. After 20 min of stirring at −10°C, copper(I) bromide · dimethylsulfide (550 mg, 2.68 mmol) and 50 mL of *n*-hexane were added. Finally the reaction mixture was sonificated for 45 minutes.

b) (4-(Ruthenocenylethynyl)-4′-ethynyltolan) (**11**): 4,4′-Diethynyltolan (**2**) (573 mg, 2.54 mmol) was dissolved in 50 mL of THF, the solution was cooled to −50°C, and *n*-butyllithium (2.0 M in hexane, 1.30 mL, 2.6 mmol) was added. Iodine (0.645 g, 2.54 mmol) was dissolved in 30 mL of THF and added. A suspension of cuproruthenocene, prepared from ruthenocene (590 mg, 2.55 mmol see above) was added, the mixture was sonificated for 30 minutes and stirred for 40 hours at room temperature. The reaction mixture was poured on a sat. aqueous solution of ammonium chloride, the resulting slurry was extracted with diethyl ether and the crude product purified by means of middle pressure chromatography (silica G-60, 220–440 mesh, *n*-hexane: diethyl ether 50:50). Two compounds were obtained: 4-(Ruthenocenylethynyl)-4′-ethynylruthenocene (**11**) (450 mg, 0.99 mmol, 39%) ^{1}H-NMR ($CDCl_3$) 3.09 (s, 1 H, $C\equiv C\underline{H}$), 4.51 (t, 2H, J = 1.5, $H_{2,5}$), 4.54 (s, 5 H, $H_{1'-5'}$), 4.82 (t, 2 H, J = 1.5, $H_{3,4}$), 7.20–7.38 (m, 8 H, H_{aryl}); ^{13}C-NMR ($CDCl_3$) 70.7, 71.8, 73.5, 83.2, 131.2, 131.4, 132.0, 132.2; IR (KBr) 3280 b,m, 3097 w, 2923 w, 2849 w, 2205 m, 1667 w, 1596 w, 1519 s, 1449 w, 1407 m, 1297 w, 1262 m, 1164 w, 1102 s, 1054 m, 1025 s, 1000 s, 918 m, 837 s, 810 vs, 652 m, 623 m, 542 s, 483 m, 448 s, 428 m; MS calcd for $C_{28}H_{18}Ru$ 455.520, found m/z 456 ($M^{+\cdot}$, 100%), and 4, 4′-Bis(ruthenecenylethynyl)tolan (**12**) (100 mg, 0.15 mmol, 6%). ^{1}H-NMR($CDCl_3$) 4.59 (t, 4H, J = 1.8, $H_{2,5,2'',5''}$), 4.62 (s, 10 H, $H_{1'-5',1'''-5'''}$), 4.89(t, 4H, J = 1.8, $H_{3,4,3'',4''}$), 7.36–7.55 (m, 8H, H_{aryl}); ^{13}C-NMR ($CDCl_3$) 70.8, 71.8, 73.6, 131.2. 131.4, 132.1; IR(KBr) 3101 b, m, 2925w, 2204s, 1519vs, 1407w, 1262w, 1181w, 1164w, 1102s, 1025w, 1000w, 837vs, 812s, 756w, 542m, 448m; MS calcd for $C_{38}H_{26}Ru_2$ 684.76, MS found m/z 684 (M^+, 10%), 455.5 ($M^{+\cdot}$, −230, 100%).

Potassium ($C_{18}H_9$-ethynylene-*p*-phenylene)triphenyl borate (13). 4,4′-Diethynyltolan (**2**) (1.58 g, 7.0 mmol) was dissolved in THF (15 mL) and the system was cooled to −60°C. In a stream of argon *n*-butyllithium (2.0 M in *n*-hexane, 3.5 mL, 7.0 mmol) was added and the system stirred for 30 min. Triphenylborane [38] (1.70 g, 7.0 mmol) was dissolved in THF (15 mL) in a separate vessel and the contents were combined at −30°C. The cooling bath was removed and the reaction mixture stirred at room temperature for 18 h. The solvent was removed at a HV pump, the yellow residue was taken up in argon-saturated water and carefully extracted with pentane:ether 80:20. Insoluble residues were separated by filtration. The aqueous phase was concentrated to the half of its volume and the product was precipitated with potassium chloride (4.7 g, 63.0 mmol). The system was further concentrated and sufficient time was given to the entire precipitation. The flaky detergens was collected with a suction filter (G3) and dried at the HV pump. Pale yellow crystals of potassium($C_{18}H_9$-ethynylene-*p*-phenylene)triphenylborate (**13**) (0.57g, 1.1mmol, 16%) were isolated. ^{1}H-NMR (CD_3CN) 7.38 (m, 12H, H_{phenyl}), 7.03 (m, 8H, $H_{\text{-}p\text{-phenylene}}$), 6.90 (m, 3H, H_{phenyl}), 3.47 (s, 1H, $C\equiv C\underline{H}$); ^{13}C-NMR(CD_3CN) 135.1, 131.7, 131.5, 126.5, 123.1; IR(KBr) 3278s ($C\equiv C—H$), 3058 w (Ar—H), 3010 w, 2964 w, 2532 w, 2213 w ($C\equiv C$), 2148 w (BPh_3), 2105 w (Ar), 1926 w, 1596 m, 1582 w, 1513 s, 1480 w, 1430 w, 1405 w, 1264 m, 1233 w, 1179 w, 1135 w, 1104 m, 1030 w, 1017 w, 949 w, 904 w, 839 s, 758 w, 745 m, 708 m, 646 m, 623 m, 546 s, 494 w, 452 w; MS calcd for $C_{36}H_{24}BK$ 506.49 (467.40, -K), MS found m/z 467 ($M^{+\cdot}$, 100%).

4-(Ferrocenylethynyl)-4′-bromobenzil (14) and 4,4′-Bis(ferrocenylethynyl) benzil (17). 4,4′-Dibromobenzil (1.28 g, 3.48 mmol) was dissolved in diethylamine (15 mL, dried over KOH). Ethynylferrocene [36] (878 mg, 4.58

mmol), bis(triphenylphosphine) palladium(II)chloride (59 mg, 0.084 mmol) and copper(I)iodide(8 mg, 0.042 mmol) were added. For reasons of homogenization, 20 mL THF were added. The reaction mixture was stirred for 18 hours, then all the volatiles were removed in vacuo. The residue was purified by means of middle pressure chromatography (Silica G-60, 220–440 mesh, 5 x 100 cm, petroleum ether: diethyl ether 50:50, flowrate: 35 mL/min). Yields: 4-(Ferrocenyl-ethynyl)-4′-bromobenzil (**14**) (1.3 g, 2.62 mmol, 75%) and 4,4′-bis(ferrocenylethynyl)benzil (**17**) (0.45 g, 0.723 mmol, 21%). Both products were recrystlized from cyclohexane. 4-(Ferrocenylethynyl)-4′-bromobenzil (**14**) : ^{1}H-NMR ($CDCl_3$) 4.12 ("t", 2 H, J = 1.8 Hz), 4.14 (s, 5 H), 4.39 ("t", 2 H, J = 1.8 Hz), 7.0 – 7.73 (m, 8 H); ^{13}C-NMR ($CDCl_3$) 69.19, 70.11, 72.07, 128.20, 128.65, 129.86, 130.47, 131.18, 131.92, 132.75; IR(KBr) 3090 w, 2925 m, 2845 m, 2200 s, 1680 s, 1670 s, 1600 vs, 1410 b,m, 1215 s, 1160 s, 1110 m, 1005 b, m, 900 m, 880 m, 820 b,m, 500 b, m; MS calcd for $C_{26}H_{17}BrFeO_2$ 497.17, MS found m/z 497 ($M^{+\cdot}$, 100%). 4,4′-Bis(ferrocenylethynyl)benzil (**17**): ^{1}H-NMR ($CDCl_3$) 4.13 (s, 5 H, $H_{1'-5'}$), 4.17 (t, 4 H, J = 1.8 Hz, $H_{2,5}$), 4.41 (t, 4 H, J = 1.8 Hz, $H_{3,4}$), 7.47–7.65 (m, 4 H, H_{aryl}),7.79–7.82 (m, 4H, H_{aryl}); ^{13}C-NMR ($CDCl_3$) 69.41, 70.07, 71.71, 129.82, 131.60; IR (KBr) 3100 w, 2930 m, 2850 m, 2205 s, 1680 vs, 1670 vs, 1600 vs, 1410 vs, 1220 s, 1160 s, 1110 m, 1010 m, 900 s, 820 b,s, 780 m, 740 m, 620 m, 500 b,m; MS calcd for $C_{38}H_{26}Fe_2O_2$ 626.06, found m/z 626 ($M^{+\cdot}$, 80%), 285 (100%, phenylethynylferrocenium cation).

4-(Ferrocenylethynyl)-4′-(3-hydroxy-methylbut-1-ynyl)benzil (15). 4,4′-Dibromobenzil (268 mg, 0.76 mmol), ethynylferrocene [36] (160 mg, 0.76 mmol), $Pd(PPh_3)_2Cl_2$ (130 mg, 0.185 mmol) as well as Cu(I)I (5 mg, 26.2 µmol) were dissolved in 10 mL of diethylamine. 30 mL of THF were added and the solution was stirred for 4 hours at room temperature. 3-Hydroxy-3-methylbut-1-yn-3-ol (100 mg, 1.19 mmol) was added to the intermediary formed solution of 4-(ferrocenylethynyl)-4′-bromobenzil and the solution was stirred for another 12 hours. The solvent was removed *in vacuo* and the residue purified by means of flash chromatography (silica G 60, 220–440 mesh, 4 × 30 cm, diethyl ether : hexane 25 : 75). Recrystallization from cyclohexane yields 4-(ferrocenylethynyl)-4′-(3-hydroxy-3-methylbut-1-ynyl) benzil (**15**) (200 mg, 0.4 mmol, 53%). mp 125°C; ^{1}H-NMR ($CDCl_3$) 2.08 (s, 6H, CH_3), 4.16 (s, 5 H, $H_{1'-5'}$), 4.21 (t, 2 H, J = 1.5, $H_{2,5}$), 4.45 (t, 2 H, J = 1.5, $H_{3,4}$), 7.74–7.90 (m, 8 H, H_{aryl}); ^{13}C-NMR ($CDCl_3$) 31.2 ($\underline{C}H_3$), 65.5, 69.5, 70.1, 129.8, 132.1; IR(KBr) 3250 b, vs, 2980 vs, 2920 vs, 2850 s, 2200 w, 2140 w, 1675 b, s, 1600 s, 1460 s, 1450 s, 1410 s, 1215 vs, 1170 b, vs, 970 vs, 960 vs, 890 s, 845 s, 725 b, m, 555 m, 455 m; MS calcd for $C_{31}H_{24}FeO_3$ 500.38, MS found m/z 500 ($M^{+\cdot}$, 7%).

4-(Ferrocenylethynyl)-4′-(trimethylsilylethynyl)benzil (16). 4,4′-Dibromobenzil (268 mg, 0.76 mmol), ethynylferrocene [36] (160 mg, 0.76 mmol), $Pd(PPh_3)_2Cl_2$(130 mg, 0.185 mmol) and Cu(I)I (5 mg, 26.2 mmol) were dissolved in diethylamine (10 mL). THF (30 mL) was added and the solution stirred for 4 hours at room temperature. Trimethylsilylacetylene (86 mg, 0.88 mmol) was added to the intermediary formed solution of 4-(ferrocenylethynyl)-4′-bromobenzil and the solution was stirred for another 12 hours. The solvent was evaporated and the residual was purified by means of chromatography (silica G-60, 220–440 mesh, 4 x 25 cm, hexane: diethyl ether 75:25). Recrystallization from cyclohexane yields 4-(ferrocenylethynyl)-4′-(trimethylsilylethynyl)benzil **(16)** (ca. 180 mg, 0.35 mmol, 46%). ^{1}H-NMR($CDCl_3$) 0.2 (s, 9 H, TMS), 4.2 (s, 5 H, $H_{1'-5'}$), 4.3 (t, 2H, J = 1.5, $H_{2,5}$), 4.5 (t, 2 H, J = 1.5, $H_{3,4}$), 7.51–7.89 (m, 8 H, H_{aryl}); ^{13}C-NMR ($CDCl_3$) 0.4 (TMS), 69.4, 77.0, 71.8, 129.6, 129.8, 131.6, 132.3 IR (KBr) 3100 w, 2980 m, 2210 m, 2160 m, 1725 b,m, 1675 b,s, 1600 vs, 1410 m, 1255 m, 1215 m, 1180 m, 1160 m, 1105 w, 850 b,vs, 765 b,s, 700 b,m; MS calcd for $C_{31}H_{27}FeO_2Si$ 515.49, MS found m/z 514 ($M^{+\cdot}$, 100%).

4,4′-Bis(ferrocenylethynyl)benzil (17). see: 4-(Ferrocenyletynyl)-4′-bromobenzil **(14)** and 4,4′-bis(ferrocenylethynyl)benzil **(17)**.

Ethynylruthenocene. a) Improved lithiation of ruthenocene with *n*-butlithium (favoring monosubstitution): Ruthenocene (1.42g, 6.15 mmol) was dissolved in 30 mL of THF, the solution was cooled to 0°C and *n*-butyllithium (1.6 M in hexane, 3.85 mL, 6.15 mmol) was added. After 30 minutes copper(I)bromide·dimethylsulfide 1.38 g, 6.73 mmol) was added, stirred for 10 min and the deep blue solution treated with 1-iodo-3-hydroxy-3-methylbut-1-yne (1.32 g, 6.3 mmol). The reaction mixture was poured on a sat. aqueous solution of ammonium chloride and extracted with diethyl ether. Purification was achieved by means of column chromatography (silica G-60, 220–440 mesh, 4 x 50 cm, 1. *n*-hexane, 2. *n*-hexane: diethyl ether 70:30, 3. *n*-hexane: diethyl ether 50:50). 1. Fraction: ruthenocene (0.78 g, 3.4 mmol, 55%); 2. fraction: 1-(3-hydroxy-3-methylbut-1-ynyl) ruthenocene (0.85 g, 2.7 mmol, 44%). Additional traces of the 1,1′-disubstituted species (<1%) were found.

b) Ethynylruthenocene: 1-(3-Hydroxy-3-methylbut-1-ynyl)ruthenocene (0.674 g, 2.15 mmol) was dissolved in 25 mL of *n*-butanol. Sodium hydroxide (350 mg) was added and the reaction mixture was refluxed for 2 h. Finally, all the volatiles were removed in vacuo and the residue was purified by means of column chromatography (Silica G-60, 220–440 mesh, 4 x 25 cm, *n*-hexane) and recrystallized from hexane to yield pure ethynylruthenocene (0.49 g, 1.9 mmol, 90%).

4-(Ferrocenylethynyl)-4′-(ruthenocenylethynyl)benzil (18). Ethynylruthenocene (240 mg, 0.94 mmol) was dissolved in diethylamine (10 mL, dried over KOH) and 4-(ferrocenylethynyl)-4′-bromobenzil **(14)** (390 mg, 0.78 mmol), bis(triphenylphosphine) palladium(II)chloride (11 mg, 15.7 μmol) as well as copper(I)iodide (5 mg, 0.026 mmol) were added. For reasons of homogenization THF (10 mL) was added. The solution was stirred for 6 hours, then all the volatiles were removed in vacuo and the residue was purified by means of chromatography (silica G-60, 220–440 mesh, 5 × 25 cm, *n*-hexane: diethyl ether 75:25, flowrate: 10 mL/min). Recrystallization from cyclohexane yields 4-(ferrocenylethynyl)-4′-(ruthenocenylethynyl)benzil **(18)** (160 mg, 0.238 mmol), 39%). ^{1}H-NMR ($CDCl_3$) 4.13 (s, 5H, $H_{1'-5'}$), 4.18 (t, 2 H, J = 2.4, $H_{2,5}$), 4.39 (t, 2 H, J = 2.4, $H_{3,4}$), 4.44 (t, 2 H, J = 1.7, $H_{2'',5''}$), 4.50 (s, 5H, $H_{1'''-5'''}$), 4.74 (t, 2H, J = 1.7, $H_{3'',4''}$), 7.32–7.82 (m, 8H, H_{aryl}); ^{13}C-NMR ($CDCl_3$) 69.41, 70.05, 70.96, 71.84, 71.99, 74.09, 129.80, 131.23, 131.58, 131.86, 132.41; IR (KBr) 3090 w, 2210 s, 1685 b,s, 1600 vs, 1220 m, 1160 m, 900 m, 850 w, 820 m, 620 w; MS calcd for $C_{38}H_{26}FeORu_2$ 671.54, MS found m/z 672 ($M^{+\cdot}$, 60%).

CONCLUSION

Elongation of tolan and benzil spacers with partially protected ethynes and phenylacetylenes as well as functionalization with metallocene, metallocenium, borate and various organic acceptor substituents provided a series of novel rigid-rod molecules. Their destination as patterns to molecular wires or materials for molecular electronics has been surveyed. The majority of structures, however, has been designed for nonlinear optical purposes. Organometallic functionalities have been incorporated in combination with distinct spacers that offer additional synthetic versatilities. The synthetic tools have entirely been discussed in earlier contributions by several authors so that only improvements in the preparation of different precursors are reported besides an innovative compilation based on the selected building-blocks. Addition-elimination reactions, direct ethynylation reactions, coupling reactions according to Hagihara, Stephens-Castro and Glaser as well as transmetallation reactions have been utilized in the synthesis of numerous application-oriented target compounds. It should be emphasized that the diversity of applied constituents and the conceptual flexibility directly affords functional macromolecules which, in general, can not be prepared from divergent homologation concepts. The presented "low-cost bridging ligands" may especially serve for mixed spacer elongation in combination with solubilizer-substituted systems which are more cumbersome to prepare. To achieve made-to-measure macromolecular structures, the modular construction as proposed turned out to be highly effective and can be adapted according to the prerequisties of sharply defined scopes.

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[1] These systems are also designated as: tolan based, diphenylacetylenes, diphenylethynyls, polyphenylpolyine, phenylacetylenes, poly(phenylacetylene), poly(phenylene-acetylenes), phenylene(ethynediyl), poly-(phenylene-ethynylene) or more generally as poly (aryleneethynylene) or aryl-ynylenes. For a recent review see: J. M. Tour, *Chem. Rev.*, **96**, 537 (1996). For CA nomenclature see for instance ref. 28b).

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