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Synthesis of novel liquid crystalline organometallic polymers

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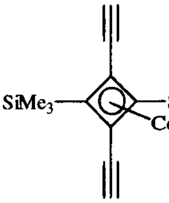
Abstract: The synthesis and some properties of organometallic homo- and copolymers carrying diethynylated π–complexes are discussed. As monomers the diethynylated derivatives of cymantrene and cyclopentadienyl(1,3-bistrimethylsilylcyclobutadiene)cobalt were utilized. Novel thermotropic nematic and lyotropic smectic liquid crystalline polymers were synthesized as copolymers of **1** and 2,5-dihexyl-1,4-diiodobenzene or 3-hexyl-2,5-diiodothiophene in a Cassar-Heck-Hagihara coupling reaction. The liquid crystalline behavior was secured by polarizing microscopy and powder X-ray diffractometry.

Introduction

Organometallic polymers hold a great future (academic) potential for the synthesis of materials with attractive properties such as liquid crystallinity, redox activity and electroresponsive behavior as well as NLO activity (1-4). In a more practical vein, organometallic fragments have been attached to polyaramides and polyphenylenesulfides improving their solubility and processability (5). Despite the broadened profile of properties and the exotic structures attainable, much less effort has been devoted towards synthesis and property assessment of organometallic polymers, in comparison to purely organic polymers.

We have an interest in synthesis and chemistry of multiply ethynylated π–complexes which led to the preparation of several diethynylated species such as **3** - **6**. They are attractive monomers in polymerization experiments (6) and/or building blocks for alkyne-bridged oligomers. With exception of **1** and **2** (7) no examples of multiply alkynylated π–complexes were known in 1992 and no generally applicable synthetic routes to such species had been described in the literature. In this contribution we wish to show the development of efficient synthetic routes to diethynylated cyclobutadiene and cyclopentadienyl complexes and their use in the synthesis of oligomers and polymers.



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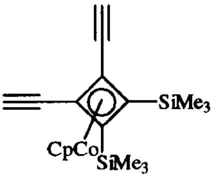

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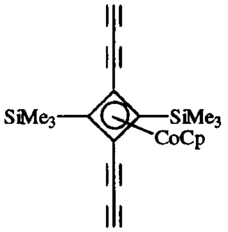

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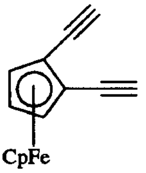

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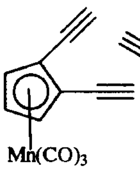

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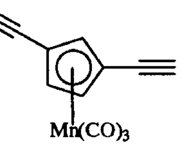

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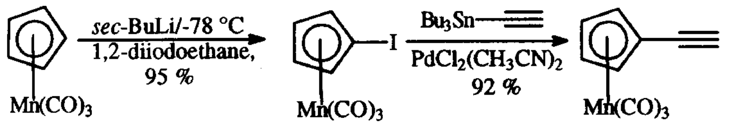
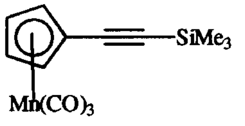
Monomer synthesis

In a landmark paper Stille and Sterzo (8) showed, that **7** could be transformed efficiently into **9** under palladium catalysis. We prepared **11** (75 %) using the same route (9). Unfortunately **11** afforded an *ortho/meta*-mixture of **12** upon metalation/iodination, which was not separable and contained a paramagnetic impurity, prohibiting even the spectroscopic characterization of the mixture **12**. Coupling with **10** led to the formation of the diethynylated moieties **13** (47 %) and **14** (26 %) which were separable by flash chromatography. Desilylation of **13** and **14** made parents **5** and **6** accessible in high yields (9). The analogous reaction sequence is applicable to the synthesis of diethynylated cyclobutadienes stabilized by

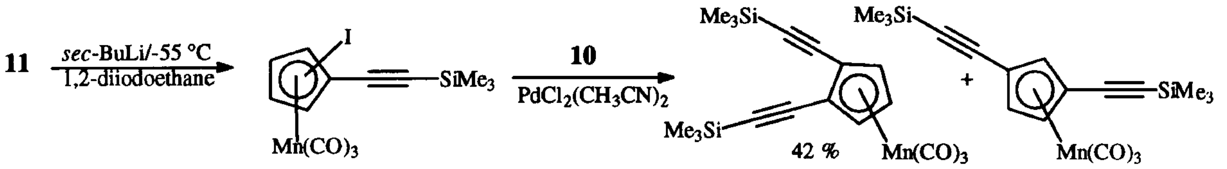
$Fe(CO)_3$, **15** and **16** (10). In contrast, to prepare 1,2-diethynylferrocene **19** it was necessary to use another route, due to the unwanted lithiation of the second ring as a side reaction: treatment of the literature known **17** with PPh_3=CHCl furnished **18** in 71 % as a mixture of three isomers. Reaction of the isomeric mixture **18** with KO*t*Bu in DMSO yielded 1,2-diethynylferrocene **19** in 46 % (11) after double dehydrohalogenation.

All of the here presented diethynyls, **4** - **6**, **15**, **16** and **19** are accessible in multigram-quantities and surprisingly stable under ambient conditions, making them candidates for the design of novel organometallic polymers.

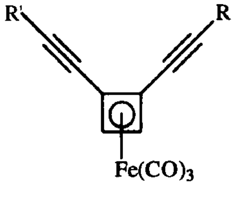


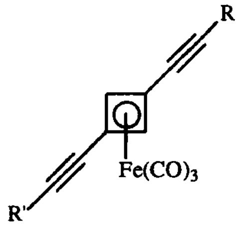


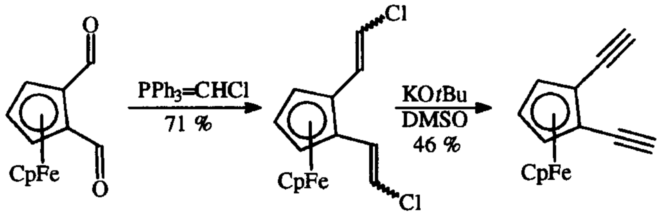
7 **8** **9** **10** **11**



12 **13** **14**





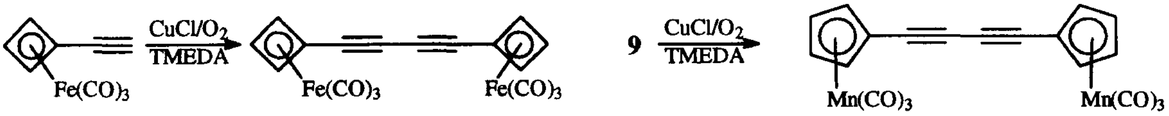


15 **16** **17** **18** **19**

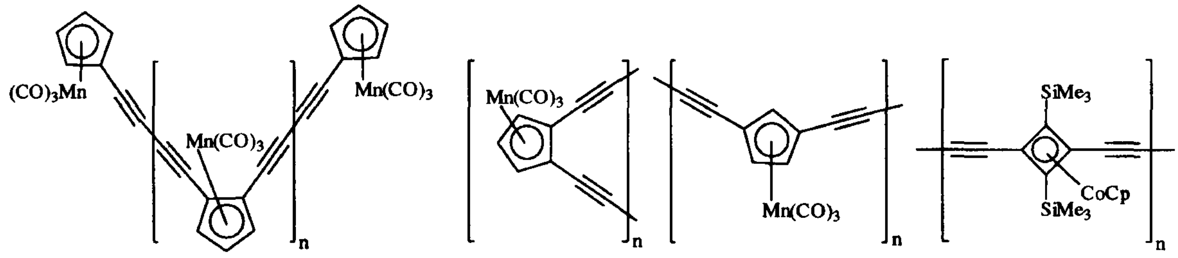
Oligomer and polymer synthesis

For the synthesis of oligomers and homopolymers of diethynylated species Glaser- or Hay-type coupling (12) were considered. It was not clear though if the organometallic alkynes would survive under the oxidative reaction conditions. Therefore we subjected **9** and **20** respectively, to the conditions of the Hay coupling and isolated in both cases the butadiynes **21** (54 %) or **22** (89 %). No oxidative decomposition of the products was observed. That suggested that the formation of oligomers and polymers would be feasible as well using this route (13). If **4** and **9** are cooligomerized, a series of oligomers **23** (n = 1 - 5) was separated (10) using preparative hplc. Omitting **4**, polymer **24** (n > 25) was observed, but no compounds having cyclic structures were obtained. In both cases, **23** and **24**, stereoisomers should occur due to the fact that the $Mn(CO)_3$-group destroys the planarity and therewith the mirror plane of the oligomers **23** (for n > 1). Surprisingly, stereoisomers were neither visible in the NMR spectra of the **23** or **24** nor distinguishable by hplc; probably the diyne bridge separates the stereocenters too far to be discerned by NMR spectroscopy.

Attempts to synthesize and characterize polymer **25** from **5** was thwarted by the complete insolubility and infusibility of the reaction product, which is not uncommon for rigid rod-like oligomers/polymers. Attempts to polymerize **15** failed, instead the obtained material rapidly decomposed under darkening (10). While it is sufficient to perform Hay coupling in the cymantrene series at 21 °C for 2 h, efforts to couple **1** under identical conditions only led to the formation of traces of **26a** (n = 1) and the reisolation of **1**. A polymer (n > 17) was obtained treating **1** in a mixture of boiling tetramethylethylenediamine and CuCl, admitting oxygen for 17 h (15). Surprisingly no crosslinked or oxidized products of *poly*-**26** were observed, despite the harsh conditions used. When the UV-vis spectrum of polymer **26** was compared to that of **1**, a considerable increase in the molar extinction coefficient as well as a pronounced bathochromic shift of the bands to 360 and 440 nm (21 and 61 nm) had occurred. In order to understand this behavior, oligomers **26** (n = 2 - 8) were synthesized (14) by conducting the oligomerization reaction of **1** in boiling butanone for only 4 h. Separation of **26** (n = 2 - 8) by preparative hplc afforded the different oligomers in yields between 2 and 6 %. The UV-vis spectrum of the heptamer **26f** is almost superimposable to that of *poly*-**26**, while the spectra of the lower oligomers show an increasing hypsochromic shift of the bands at 360 and 440 nm (*poly*-**26**) with smaller values of n. Oligomers **26** carry terminal alkyne groups, thus will be able to function as bridges between electroactive or chromophoric groups such as ferrocenes, anthracenes etc.



20 **21** **22**

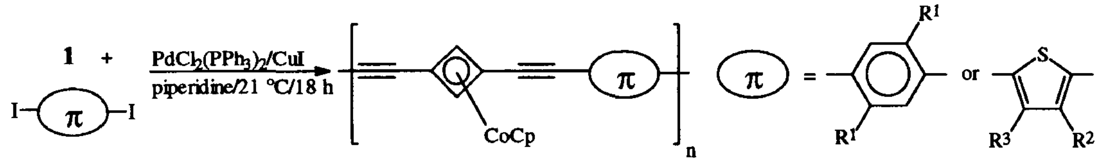


23 **24** **25** **26**

Phase behavior of the copolymers containing 1 and benzene and thiophene units (6)

First attempts to couple dibromobenzene with **1** under typical Heck-Cassar-Sonoshigara-Hagihara-conditions (15) failed. Only if **1** was treated with diiodobenzenes or diiodothiophenes **27** using a variant of this reaction developed by Alami and Linstrumelle (16) the formation of the copolymers **28** occurred in yields between 74 and 86 %. So the use of *diiodides* and piperidene as base were the key to conduct a successful (co)polymerization.

Copolymers **28** are yellow-brownish film forming substances, stable to atmospheric conditions for prolonged periods of time. Due to the rigid rod nature of the polymers it was suspected that they might form lyotropic and/or thermotropic (nematic) mesophases. For solutions of the phenylene copolymers **28a** - **c** in dichloromethane, nematic *schlieren* textures and/or Maltese crosses were visible under crossed polarizers after slow evaporation of the solvent, indicating the presence of a frozen lyotropic liquid crystalline (lc) phase. While there are several lyotropic organometallic lc systems known (1), thermotropic



27 **28** **a-c** **d-h**

Table 1: Substitution pattern, yields and substituent keys for polymers **28**

28	R^1	R^2	R^3	yield	M_n(10^3)	M_w(10^3)	P_n[a]
a	H			86 %	4.31	7.41	18
b	Hexyl			74 %	5.13	13.1	18
c	Dodecyl			79 %	4.91	20.1	12
d		H	H	78 %	8.10	12.0	18
e		Hexyl	H	82 %	14.0	30.0	27
f		Dodecyl	H	79 %	5.18	11.4	15
g		Hexyl	Hexyl	81 %	9.60	29.0	15
h		Dodecyl	Dodecyl	81 %	13.4	35.3	42

[a] P_n: Degree of polymerisation;

organometallic main chain polymers were not described in the literature: polymer **28b** formed an isotropic film when casted to a glass slide by fast evaporation of dichloromethane. Upon heating to 165 °C a *schlieren* texture was observed suggesting the development of a thermotropic nematic lc phase. This was corroborated by differential thermal analysis indicating a structural change at 155 °C. Temperature dependent powder diffractometry proved, that above 160 °C every crystalline order disappeared, supporting the results obtained by microscopy and differential thermal analysis. While the thiophene copolymers **28d-h** do not exhibit thermotropic mesophases, all of them formed lyotropic lc phases as was evidenced by polarizing microscopy. While **28d** and **28f-h** display typical nematic *schlieren* textures or maltese crosses, **28e** was particular, as it showed a brush- or fan-type texture normally expected in non-polymeric smectic lc phases. Electron microscopy revealed that the features observed as brushes in the optical micrograph were composed of ordered polymer lamellae, where the diameter of a lamella was determined to be approximately 30 nm, corresponding to a single macromolecule **28e** with a degree of polymerisation (P_n) of roughly 25 - 30. A similar P_n was obtained from gel permeation chromatography. The unusual lyotropic smectic phase behavior was corroborated by powder diffractometry as well as by electron diffraction. Polymer **28e** is the first organometallic main chain polymer exhibiting smectic behavior. It can be explained by assuming that the Cp-cobalt fragments of different chains are correlated in two dimensions, despite the fact that the macromolecules themselves are probably ordered in a nematic fashion (17,18).

Conclusion

In conclusion we have been able to show, that the with the construction of diethynylated π-complexes a series of monomers is accessible for the synthesis of hitherto unknown polymers, of whom the copolymers of structure **28** show attractive lc behavior which is depending on the used comonomers **27**. In the future we will expand the chemistry of multiply ethynylated cymantrenes towards the synthesis of polymers which are peralkynylated, water soluble, redox active or carry mesogenic groups to display desired material science properties.

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