Synthesis of Cymantrene-Containing Organometallic Polymers Using the Suzuki Coupling

Sepas Setayesh and Uwe H. F. Bunz*

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

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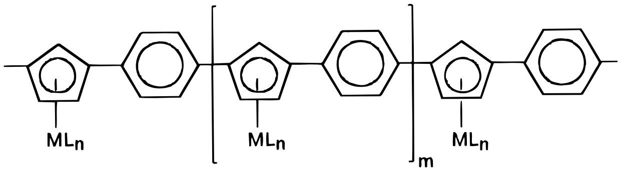
Summary: The synthesis of a novel rigid-rod phenylene−cymantrenylene copolymer using the Suzuki coupling as the polymer forming reaction is reported.

The Suzuki coupling is the reaction of an arylboronic acid with an aromatic halide (preferably a bromide) catalyzed by Pd(0) to give the corresponding biaryl[1] in excellent yields. While it was developed for the construction of natural products containing biaryl units,[2] this coupling reaction turned out to be efficient for the synthesis of rigid-rod polyarylenes, particularly of the poly-*p*-phenylene type.[3] The difunctional coupling reactions result in degrees of polymerization up to $P_n \approx 100$.[4a,5] Organic rigid-rod polymers are valuable in materials science for different reasons, including the design of novel liquid crystalline phases[4b] and stable and transferable mono- and multilayers,[4c] as well as for NLO and similar applications.[4d]

The direct Suzuki coupling of arenes ligated by organometallic fragments, in contrast, is rare and includes only a couple of examples.[5−7] None of these have been used for the synthesis of rigid-rod organometallic polymers, which are emerging as attractive candidates for many applications in materials science.[8−10] The synthesis of rigid-rod type polymers with 1,3-disubstituted cyclopentadienyl complexes introduced as links in the main chain was hampered by the difficult synthesis of the corresponding monomers, so that polymers of the structure **A** are virtually unknown. For the synthesis of a cymantrenylene−phenylene copolymer, for example, the corresponding 1,3-dihalogenated cymantrenes are obtained only with great effort. In this paper we describe a general route for the synthesis of 1,2,3-trifunctionalized cymantrene monomers and their use in the synthesis of the corresponding polymers.



A

Monometalation of cymantrene with *sec*-BuLi is a facile process.[11] The ring metalation can be *ortho*-directed by substituents such as acetal or alkyne groups.[12] At first direct double metalation of the cymantrene nucleus (−78 °C, 2 h, THF) with 4.5 equiv of *sec*-BuLi and subsequent workup with chlorotrimethylsilane was attempted (in contrast to Gladysz's CpRe(NO)PPh$_3$Cl complex); no defined product could be isolated, however.[13] We anticipated that in the synthesis of a rigid-rod organometallic polymer with structure **A**, the monomer(s) would require solubilizing group(s). Acetals derived from formylcymantrene are easily prepared and should allow by virtue of their *ortho*-directing power the synthesis of 2,5-disubstituted cymantrenes. Reaction of the acetal **1** (prepared from formylcymantrene and 2,2-dimethylpropanediol under the influence of catalytic amounts of TsOH)[14] with 4.5 equiv of *sec*-BuLi for 1 h at −78 °C in THF and subsequent workup with chlorotrimethylsilane permitted the isolation of a yellow crystalline material in 71% yield (mp 92 °C, after chromatography over flash silica gel).[15] The ^{1}H NMR spectrum of this compound displayed only one signal in the Cp region at δ 4.76 (2 H) and one signal in the region expected for TMS groups (δ 0.25, 18 H). The corresponding ^{13}C NMR spectrum showed 10 signals, of which three were attributed to the cyclopentadienyl ring, *viz.* the ones at δ 89.3 (s, 2 C) and 92.2 (d, 2C) and the singlet at 118.0 (1 C). Diagnostic is the band at δ 225.3, attributed to the CO groups. The magnetic

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[14] Synthesis of **1**: formylcymantrene (24.6 g, 106 mmol), 2,2-dimethylpropan-1,3-diol (54.0 g, 519 mmol), and *p*-toluenesulfonic acid (2.00 g, 8.40 mmol) are dissolved in 600 mL of toluene. This solution is heated to reflux for 4 h using a Dean−Stark trap. The solvent is evaporated and the crude product dissolved in 1 L of pentane. Washing the organic phase with 300 mL of the methanol/water (1:1), drying over MgSO$_4$, and evaporating the solution give rise to the isolation of 32.2 g (95%) of **1** after chromatography over silica gel (pentane/dichloromethane; 1:1); mp 71−72 °C. IR (KBr): ν 3114, 2966, 2858, 2842, 2018, 1925, 1394, 1108 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.75 (s, 3 H), 1.24 (s, 3 H), 3.52 (d, J = 11 Hz, 2 H), 3.68 (d, J = 11 Hz, 2 H), 4.63 (s, 2 H), 4.97 (s, 2 H), 5.09 (s, 1 H). ^{13}C NMR (50 MHz, CDCl$_3$): δ 21.7, 22.9, 30.1, 77.4, 81.0, 82.6, 96.6, 102.0, 224.7. MS (EI, 70 eV): m/z (%) 318 (11, M$^+$) 262 (2, M − 2CO), 234 (10, M − 3CO), 204 (100). Anal. Calcd for C$_{14}$H$_{15}$O$_5$Mn (318.25): C, 52.8; H, 4.8. Found: C, 52.8; H, 4.8.

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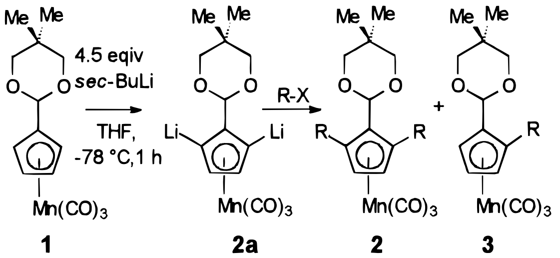
Table 1. Yield and Substituent Key for 2 and 3

2, **3**	substituent	yield of **2** (%)	yield of **3** (%)	Σ of yield (%)
a	Li			
b	$SiMe_3$	71	5	76
c	SMe	53	32	85
d	I	77	3	80

resonance data exclude the structure **3b**, which would have a lower symmetry, and clearly indicated the formation of the bis-silylated **2b** (R = TMS). The proposed structure for this product was corroborated by the mass spectroscopic analysis displaying the molecular ion at *m*/*z* 462 followed by a signal at *m*/*z* 378 assigned to the fragment M − 3CO.

Using column chromatography, we were also able to isolate the mono(trimethylsilyl)-substituted cymantrene **3b** in a yield of 5%.[15] The reaction of **2a** with methyl disulfide gave rise to the isolation of a 53% yield of **2c** and 32% of the mono(methyl thioether) **3c**. Treating **2a** with diiodoethane led to the isolation of the desired diiodide **2d** in 77% yield, while the corresponding monofunctionalized **3d** had formed in 3% yield. The direct precursor to the trisubstituted cymantrenes **2b**−**d** must have been the corresponding dilithio compound **2a**. Multiply lithiated cymantrenes have been previously reported by Winter, obtained during studies of metal−metal exchange reactions.[16] In another study performed by Sünkel,[17] the formation of di- or multilithiated species during a halogen−metal exchange involving pentabromocymantrene was discounted and a stepwise halogen metal-exchange-functionalization process was invoked instead. The results of our metalation experiment are the first to clearly demonstrate that the cymantrene nucleus can be lithiated doubly in a 1,3-selective fashion, leading now to the facile synthesis of 1,2,3-trisubstituted cymantrenes.

Scheme 1



The synthesis of iodides **2d** and **3d** allowed us to explore the Suzuki coupling reaction of **3d** with the

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(15) Double metalation of **1**, synthesis of **2d**: acetal **1** (5.00 g, 15.7 mmol) was dissolved in 100 mL of water and oxygen-free THF and the solution cooled to −78 °C. To this solution was added *sec*-BuLi (54.0 mL, 1.3 mol L^{-1} in cyclohexane, 70.7 mmol, 4.50 equiv). The solution, which darkened considerably, was stirred for 1 h at this temperature and then reacted with a solution of 1,2-diiodoethane (27.0 g, 94.2 mmol) in 50 mL of THF. Considerable evolution of gas accompanied this process. After 15 min the reaction mixture was warmed to 21 °C; aqueous workup and washing of the organic phase with sodium thiosulfate solution resulted in the isolation of 6.91 g (77%) of **2d** after chromatography over silica gel (pentane/dichloromethane; 4:1) and, as a second fraction, 207 mg (3.0%) of the monoiodide **3d**. **2d**: mp 121−122 °C; IR (KBr) ν 2963, 2850, 2017, 1956, 1932, 1391, 1115 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.81 (s, 3 H), 1.43 (s, 3H), 3.61 (d, J = 11 Hz, 2 H), 3.84 (d, J = 11 Hz, 2 H), 4.96 (s, 2 H), 5.11 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.8, 23.7, 30.0, 43.9, 78.0, 91.1, 99.5, 101.7, 223.6; MS (EI, 70 eV) *m*/*z* (%) 570 (10, M^+), 514 (1, M − 2CO), 486 (34, M − 3CO), 456 (28). Anal. Calcd for $C_{14}H_{13}O_5MnI_2$ (570.04): C, 29.5; H, 2.3. Found: C, 29.6; H, 2.3. **3d**: mp 95−96 °C; IR (KBr) ν 2959, 2851, 2024, 1934, 1393, 1109 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.77 (s, 3 H), 1.24 (s, 3 H), 3.62 (m, 4 H), 4.67 (s, 1 H), 4.91 (s, 1 H), 4.96 (s, 1 H), 5.11 (s, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.7, 23.0, 30.1, 46.2, 77.8, 81.7, 82.2, 89.1, 97.8, 103.6, 224.1; MS (EI, 70 eV) *m*/*z* (%) 444 (8, M^+), 388 (2, M^+ − 2CO), 360 (23, M^+ − 3CO), 330 (73). Anal. Calcd for $C_{14}H_{14}O_5MnI$ (444.10): C, 37.9; H, 3.2. Found: C, 37.7; H, 3.0. In a similar way, starting from **1** (1.00 g, 3.15 mmol), *sec*-BuLi (11.0 mL, 14.2 mmol), and chlorotrimethylsilane (1.70 g, 15.8 mmol), the two silylated cymantrenes **2b** (1.00 g, 71%, mp 92 °C) and **3b** (61 mg, 5.0%) were obtained as crystalline yellow materials. **2b**: IR (KBr) ν 2954, 2902, 2847, 2007, 1937, 1918, 1245, 1133 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.25 (s, 18 H), 0.78 (s, 3 H), 1.26 (s, 3 H), 3.51 (d, J = 11 Hz, 2 H), 3.69 (d, J = 11 Hz, 2 H), 4.76 (s, 2 H), 5.12 (s, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.7, 22.1, 23.7, 30.1, 77.2, 89.3, 92.2, 99.0, 118.0, 225.3; MS (EI, 70 eV) *m*/*z* (%) 462 (10, M^+), 378 (18, M − 3CO), 348 (100). Anal. Calcd for $C_{20}H_{31}O_5MnSi_2$ (462.57): C, 51.9; H, 6.8. Found: C, 51.9; H, 6.6 **3b**: IR (KBr) ν 2959, 2850, 2020, 1928, 1474, 1396, 1123 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.26 (s, 9 H), 0.77 (s, 3 H), 1.24 (s, 3 H), 3.61 (m, 4 H), 4.72 (s br, 2 H), 5.09 (s br, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.1, 21.8, 23.1, 30.1, 77.4, 82.3, 83.4, 86.2, 91.3, 97.6, 110.4, 224.9; MS (FD) *m*/*z* (%) 390 (100, M^+). Anal. Calcd for $C_{17}H_{23}O_5MnSi$ (390.43): C 52.3; H, 5.9. Found: C, 52.5; H, 5.9. In a similar way **2c** (684 mg, 53%; mp 106 °C) and **3c** (367 mg, 32%; mp 63−65 °C) are obtained after chromatography (aluminum oxide, pentane/dichloromethane 9:1). **2c**: IR (KBr) ν 2958, 2925, 2849, 2019, 1935, 1122, 1020 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.79 (s, 3 H), 1.27 (s, 3 H), 2.27 (s, 6 H), 3.62 (d, J = 11 Hz, 2 H), 3.78 (d, J = 11 Hz, 2 H), 4.68 (s, 2 H), 5.41 (s, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 17.8, 21.6, 22.9, 29.9, 77.7, 79.0, 97.5, 98.5, 103.6, 223.7; MS (EI, 70 eV) *m*/*e* (%) 410 (11, M^+), 326 (38, M − 3CO), 311 (28). Anal. Calcd for $C_{16}H_{19}O_5MnS_2$ (410.39): C, 46.8; H, 4.7; S, 15.6. Found: C, 46.7; H, 4.6; S, 15.7. **3c**: IR (KBr) ν 2959, 2928, 2852, 2021, 1933, 1111, 1021 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.77 (s, 3 H), 1.25 (s, 3 H), 2.27 (s, 3 H), 3.67 (m, 4 H), 4.61 (s, 1 H), 4.73 (s, 1 H), 5.08 (s, 1 H), 5.25 (s, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 18.6, 21.6, 22.9, 30.0, 77.6, 79.4, 82.1, 82.6, 96.6, 101.7, 102.2, 224.2; MS (EI, 7 eV) *m*/*z* (%) 364 (12, M^+), 280 (22, M^+ − 3CO), 250 (80). Anal. Calcd for $C_{15}H_{17}O_5MnS$ (364.30): C, 49.5; H, 4.7; S, 8.8. Found: C, 49.9; H, 4.8; S, 8.6.

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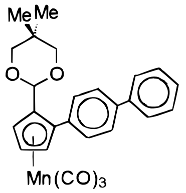
(18) Suzuki couplings, synthesis of **4**: **3d** (200 mg, 0.450 mmol), biphenylboronic acid (118 mg, 0.596 mmol), and Pd(dppfe)Cl_2 (19 mg, 23 mmol) are dissolved in 20 mL of degassed THF. Na_2CO_3 (2 M solution in water, 5 mL) is added and the solution is heated under argon to reflux for 3 days. Aqueous workup gives rise to the isolation of 164 mg (77%) of **4** after chromatography over silica gel (pentane/dichloromethane; 7:3). **4**: mp 139−140 °C; IR (KBr) ν 2956, 2929, 2850, 2019, 1927, 1102 cm^{-1}; ^1H NMR (200 MHz, acetone-d_6) δ 0.79 (s, 3 H), 1.29 (s, 3 H), 3.69 (m, 4 H), 4.94 (s, 1 H), 5.33 (s, 3 H), 7.55 (m 9 H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 21.8, 23.2, 30.3, 77.9, 79.3, 83.8, 84.4, 97.0, 100.5, 105.0, 127.3, 127.3, 128.0, 129.3, 130.0, 132.0, 140.7, 141.2, 224.9; MS (EI, 70 eV) *m*/*z* (%) 470 (3, M^+), 386 (15, M − 3CO), 355 (73). Anal. Calcd for $C_{26}H_{23}O_5Mn$ (470.40): C, 66.4; H, 4.9. Found: C, 66.2; H, 4.9. Synthesis of **5**: **2d** (400 mg, 0.702 mmol), biphenylboronic acid (354 mg, 1.80 mmol), and $Pd(PPh_3)_4$ (41 mg, 43 μmol) were dissolved in 30 mL of degassed DMF. Na_2CO_3 (2 M, 5 mL) was added, and the solution was heated under argon to 80 °C for 3 days. Aqueous workup gives rise to the isolation of 371 mg (80%) of **5** after chromatography over silica gel (pentane/dichloromethane, 7:3). **5**: mp 152 °C; IR (KBr) ν 2959, 2932, 2855, 2024, 1923, 1112 cm^{-1}; ^1H NMR (200 MHz, acetone-d_6) δ 0.73 (s, 3 H), 1.14 (s, 3 H), 3.58 (d, J = 13 Hz, 3 H), 3.66 (d, J = 13 Hz, 2 H), 5.29 (s, 2 H), 5.32 (s, 1 H), 7.55 (m, 10 H), 7.77 (d, J = 12 Hz, 4 H), 7.84 (d, J = 11 Hz, 4 H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 22.5, 24.3, 30.5, 79.1, 83.1, 98.2, 99.7, 107.3, 127.4, 127.8, 128.3, 129.6, 131.6, 132.9, 141.2, 141.7, 225.5; MS (FD) *m*/*z* (%) 622 M^+. Anal. Calcd for $C_{38}H_{31}O_5Mn$ (622.60): C, 73.3; H, 5.0. Found: C, 73.3; H, 5.0. Polymerization reactions were carried out as follows. Synthesis of **7a: 2d** (300 mg, 0.526 mmol), Na_2CO_3 (2 M, 5 mL), and $Pd(PPh_3)_4$ (30 mg, 26 μmol) were dissolved in 10 mL of oxygen-free DMF. The solution was heated to 40 °C for 7 days. 1,4-Phenylenediboronic acid (89.5 mg, 0.540 mmol) was dissolved in 10 mL of degassed DMF and was added to this solution over 5 days. After aqueous workup the polymer was precipitated into methanol and pentane: yield 166 mg (80%); IR (KBr) ν 2958, 2932, 2869, 2019, 1937, 1174 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 0.71 (s, 3 H), 1.10 (s, 3 H), 3.52 (d, J = 11 Hz, 2 H), 3.71 (d, J = 11 Hz, 2 H), 5.02 (s, 2 H), 5.23 (s, 1 H), 7.69 (s, 4 H), ^{13}C NMR (75 MHz, CD_2Cl_2) δ 22.1, 24.0, 30.1, 78.7, 83.1, 98.3, 99.1, 106.2, 130.4, 133.3, 225.1. Anal. Calcd for $C_{20}H_{17}O_5Mn$ (392.29): C 61.2; H, 4.4. Found: C, 58.6; H, 4.6. Synthesis of **7b**: same procedure as described for **7a**, using 2,5-dihexyl-1,4-phenylenediboronic acid (180 mg, 0.54 mmol). The polymer formed was precipitated into methanol: yield of **7b** 208 mg (77%); IR (KBr) ν 2955, 2928, 2856, 2018, 1935, 1106 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.70 (s, 3 H), 0.90 (s b, 6 H), 1.14 (s, 3 H), 1.27 (m, 12 H), 1.60 (m, 4 H), 2.64 (s b, 4 H), 3.15 (s b, 2 H), 3.31 (s b, 2 H), 4.86 (s b, 3 H), 7.36 (s, 2 H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 14.1, 15.1, 21.6, 22.7, 29.2, 30.3, 31.9, 32.8, 78.0, 83.9, 96.7, 102.6, 107.9, 130.4, 135.6, 139.3, 225.1. Anal. Calcd for $C_{32}H_{41}O_5Mn$ (560.61): C, 68.6; H, 7.32. Found: C, 67.1; H, 7.82.

commercially available biphenylboronic acid and Pd(dppfe)Cl_2 in a THF/water/$\mathrm{Na_2CO_3}$ mixture for 3 days at 80 °C. This protocol gave rise to the isolation of the desired coupling product **4** in 72% yield; reaction of the diiodide **3d** with biphenylboronic acid acid—as a model reaction for the synthesis of the desired polymers—yielded the corresponding bis(biphenylated)cymantrene **5** in 80% yield.



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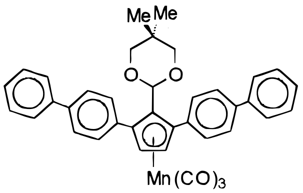

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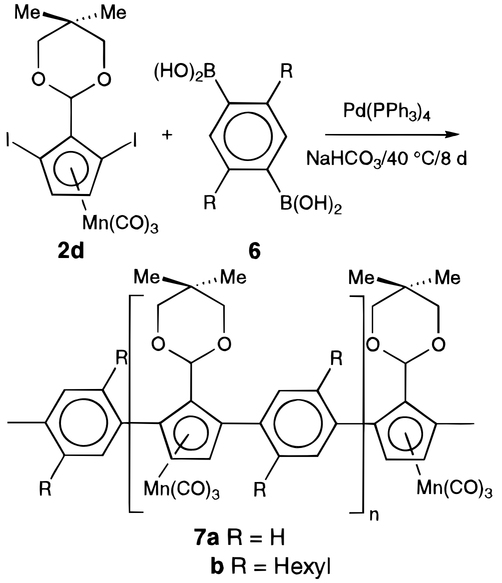
1,4-Phenylenediboronic acid can also be coupled with **2d** under the influence of 2.5 mol % Pd(dppfe)Cl_2 to form polymer **7a** in 80% yield after precipitation from methanol and pentane. The polydispersity $M_\mathrm{w}/M_\mathrm{n}$ of the material was determined by gel permeation chromatography to $D_\mathrm{n} = 6.0$ with $M_\mathrm{n} = 1.2 \times 10^4$ (corresponds to a degree of polymerization D_p of $\sim$30 with regard to the phenylene cymantrenylene unit, suggesting that 60 bonds have been found during the polymerization). The observed polydispersity is relatively high but is not without precedence[4b] for a polycondensation reaction, probably due to partial catalyst decomposition or alteration, and the material (**7a**) has the expected constitution, as can be seen by its ^{13}C NMR spectrum. Eleven signals are observed; at δ 22.1 and 24.0 the two quartets for the two methyl groups can be found and the connecting quarternary carbon emerges at δ 30.1, while the $\mathrm{CH_2{-}O}$ and the $\mathrm{CH{-}O_2}$ groups appear at δ 78.7 and 106.2, respectively. The group of lines appearing at δ 83.1, 98.3, and 99.1 are assigned to the cyclopentadienyl ligand, while the aromatic carbons were recorded at 130.4 and 133.3 ppm. The signal assigned to the three CO groups at δ 225.1 shows that the cymantrene units did not degrade in the course of the reaction. Only one set of signals, even though considerably broadened, was observed, despite the fact that the polymer perhaps is formed as a mixture of diastereomers, caused by the presence of the symmetry-breaking $\mathrm{Mn(CO)_3}$ group. The benzene-1,4-diyl unit resembles the bridging butadiyne-1,4-diyls, which were also found to efficiently isolate the stereoactive cymantrene units of our recently prepared linear fullerenyne segments.[12a]

Scheme 2



The polymerization reaction of **2d** can be carried out as well with 2,5-dihexyldiboronic acid, giving rise to the isolation of the copolymer **7b** with hexyl side chains. The M_n and polydispersity D_p values are similar (11×10^3, 6.4) to those of the polymer **7a**, indicating that the presence of the hexyl groups does not decrease the efficiency of the polymer formation.

In conclusion, we have been able to show that, starting from the acetal **1**, 2,5-disubstituted cymantrenes can be obtained by a double-metalation/electrophilic functionalization strategy. *Inter alia*, the corresponding 2,5-diiodide **2d** was synthesized *via* this route and used to build benzene−cymantrenylene copolymers by the Suzuki coupling. Thereby, we obtained the first rigid-rod organometallic polymers containing cymantrene units in the backbone. The outlined approach should be transferable to the synthesis of other conjugated all-carbon-backbone polymers carrying Cp complexes in the main chain. Further investigation into the scope of the coupling reaction with different Cp complexes as well as the material properties of these unusual polymers will be reported in the future.

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