SHORT COMMUNICATION

Suzuki-Coupling of $Cp^*Ru(\textit{para}\text{-}C_6H_4Br_2)$ with Phenyl Boronic Acid: A Model Reaction for the Synthesis of Organometallic Polymers[☆]

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Received May 22, 1996

Key Words: Suzuki coupling / π Complexes, organometallic / π Complexes, dihaloarene / Ruthenium complexes

The synthesis of a terphenyl derivative complexed by the cationic moiety Cp^*Ru^+ by Suzuki coupling of $[Cp^*Ru(BrC_6H_4Br)]OTf$ with phenyl boronic acid under catalysis of $Pd(PPh_3)_4$ in a DME-water mixture at 85 °C in quantitative yield is reported. The stable coupling product **3** was characterized by X-ray crystal structure analysis.

The formation of C–C bonds is one of the most fundamental processes both in organic and in organometallic chemistry. In recent years transition metal catalyzed C–C coupling reactions have been increasingly utilized and developed. Their popularity arises from a combination of high efficiency under mild conditions and the great variety of functional groups that are tolerated[1]. The Suzuki reaction has become a particularly valuable tool for the linking of arenes in both organic synthesis and polymer chemistry[2–5]. We are interested in organometallic polymers showing promising properties difficult to obtain for organic materials. The synthetic access to this type of structure is restricted, though, and fueled our interest to extend methodologies applied successfully for carbon-carbon bond forming reactions in organic chemistry to organometallic systems[6]. However, the coupling of an organometallic halide with an aromatic boronic acid is rare and only involved chromium tricarbonyl substituted arenes[4b,c]. The question as to whether it is possible to perform such a coupling without decomposition of other organometallic moieties has not been answered up to now. In this paper we report on the successful Suzuki coupling of a ruthenium complexed dibromobenzene with phenyl boronic acid.

The dibromide **1** is obtained in a 49% yield by reacting 1,4-dibromobenzene with $Cp^*Ru(CH_3CN)_3^+OTf^-$[7–8] (**2**) in dichloromethane. This reaction is analogous to the synthesis of the corresponding 1,4-dichloro derivative recently described by Fagan et al.[9]. Dibromide **1** is an air and water stable white crystalline material.

Compound **1** was reacted with phenyl boronic acid and catalytic amounts of $(PPh_3)_4Pd$ under various conditions shown in Table 1.

If the reaction was carried out in solvent mixtures reported in the literature (tetrahydrofuran/H_2O or toluene/H_2O) only traces of the coupling product **3** were obtained. Using DMF/H_2O as solvent improved the yield to 38%. A mixture of dimethoxyethane (DME) and H_2O turned out to be a superior choice giving quantitative yields of **3**. We attribute the solvent dependence of the yield of **3** to the better solubility of **1** in the DME/H_2O mixture in comparison to the much less polar mixtures of THF/toluene/H_2O.

The coupling product **3** was obtained as a colorless, crystalline solid. It is air-stable and soluble in common organic solvents such as toluene, ethanol and dichloromethane.

Scheme 1

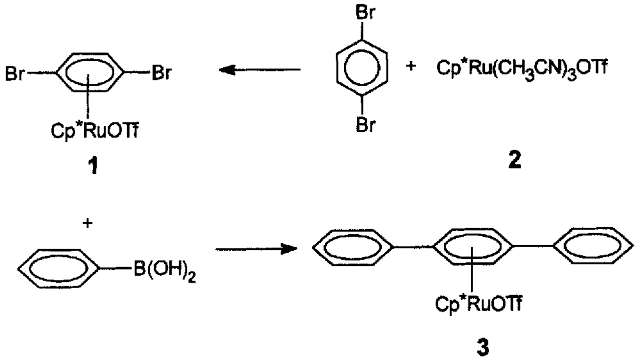
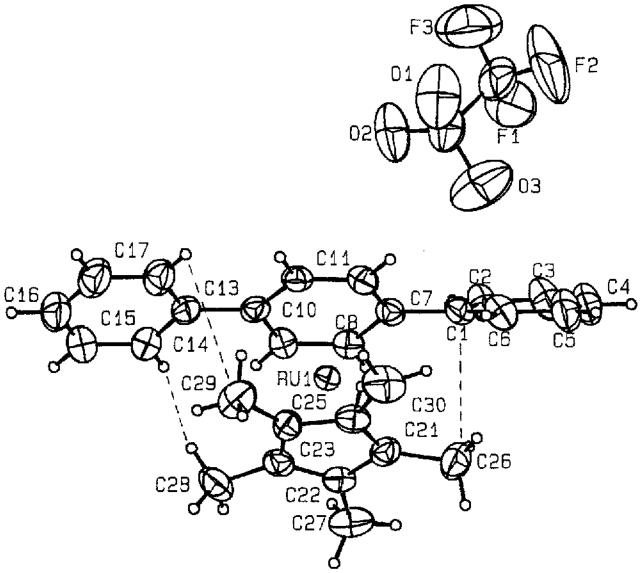


Table 1. Reaction conditions for the synthesis of complex **3** from **1** and phenyl boronic acid $[C_6H_5B(OH)_2]$

solvent	solvent ratio	base	reaction time [d]	temperature [°C]	yield [%]
THF/ H_2O	1 : 1	Na_2CO_3	1	80	0
THF/toluene/H_2O	1 : 1 :1	Na_2CO_3	2	120	11
THF/toluene/H_2O	2 : 2 : 1	Na_2CO_3	3	120	12
DMF/H_2O	3 : 2	Na_2CO_3	3	80	38
DMF/H_2O	3 : 2	$NaHCO_3$	2	80	38
DME/H_2O	3 : 2	Na_2CO_3	3	80	99
DME/H_2O	3 : 2	$NaHCO_3$	3	80	98

The molecular constitution was corroborated by an X-ray crystal structure analysis (Figure 1). As expected, the Cp*Ru moiety is bound to the central ring of the terphenyl unit. Two adjacent phenyl rings are nearly coplanar, while the third ring is twisted at an angle of 39.7° with respect to the planar biphenyl unit. This conformation is noteworthy in view of the results of X-ray crystal structure analyses of oligo-*para*-phenylenes: Unsubsituted oligophenylenes usually exhibit a torsion angle of about 21°[10]. Coplanar arrangements are absent owing to unfavorable steric interactions. In **3** the coplanar arrangement of the two phenyl groups could be understood to be forced by steric interactions of the two methyl substituents on the Cp* ligand indicated in Figure 1. Rotation about the C–C single bond of this "local" biphenyl group would lead to several nonbonding interactions between Cp* moiety

Figure 1. ORTEP plot of **3** indicating possible steric interactions



and the *ortho* hydrogens. The planar arrangement could also be explained by delocalization of the partial charge of the terphenyl unit in the π complex. In the case of the twisted ring, only one Cp* methyl group is located under the phenyl ring in a manner that does not interfere with the *ortho* hydrogens; thus the phenyl ring may twist out of plane. The distances from the metal atom to the center of the phenyl ring (1.85 Å) and the Cp* ring (1.71 Å) are in the range typically found for such complexes. The bond lengths and angles are consistent with literature values.

In conclusion we have shown that the coupling of the complexed dibromobenzene **1** under Suzuki-conditions affords the corresponding coupled product **3** in moderate to excellent yields. The dibromide **1** represents a monomer for the synthesis of organometallic poly-*para*-phenylenes containing Cp*Ru fragments. Such polymers should have interesting stereochemical as well as electronic properties.

We thank Profs. *G. Wegner* and *K. Müllen* for generous support. U. H. F. B. thanks the *DFG* for a Habilitandenstipendium (1994–1996).

Experimental

General: All reactions were carried out in an inert atmosphere (argon) using Schlenk techniques. Solvents were dried and distilled under argon before use: tetrahydrofuran was distilled from sodium/potassium alloy, ethyl ether from sodium dispersion, and dichloromethane from CaH_2. Water free acetonitrile was used as purchased from Aldrich (<0.005% H_2O), dimethoxyethane was purchased from Fluka. Water was degassed before use. All other chemicals were purchased from Strem, Aldrich and Fluka and used without further purification. The starting materials $(Cp^*RuCl_2)_2$, $[Cp^*RuCl]_4$ and $[Cp^*Ru(CH_3CN)_3]CF_3SO_3$ **2** were prepared according to procedures described in the literature[6–8]. – IR-spectra were measured using a Perkin-Elmer FT-IR spectrometer paragon 1000. – ^1H and ^{13}C NMR spectral data were obtained using a Varian Gemini 200 spectrometer at 200 MHz and a Bruker AC 300 spectrometer at 300 and 75 MHz. – Mass spectrometry was carried out with a field desorption experiment using a ZAB2-SE-FPD.

Ruthenium Complexed Dibromobenzene **1**: This compound is prepared similar to the known dichloro derivative[9]. A Schlenk flask is charged with 1.89 g (3.70 mmol) $[Cp^*Ru(CH_3CN)_3]CF_3SO_3$) and 40 ml of dichloromethane. A solution of 1.40 g (5.93 mmol) dibromobenzene in 40 ml of dichloromethane is added via a flex needle. The reaction mixture is stirred for 12 hours at room temperature. The solution is then filtered. The addition of 80 ml of ethyl ether to the filtrate leads to precipitation of **1**, which is collected by filtration. More product is obtained by further addition of 80-ml-portions of hexane to the filtrate and subsequent precipitate isolation. The solid is recrystallized from 2-propanol and dried in vacuo to yield 1.12 g of **1** (49%); m.p. 287 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 3065 cm^{-1}, 2969, 2920, 1734, 1718, 1700, 1684, 1654, 1560, 1541, 1508, 1474, 1457, 1431, 1391, 1329, 1272, 1258, 1223, 1165, 1080, 1064 (C–Br), 1030, 996, 663, 756, 716, 638, 574, 520, 456. – ^1H NMR ($CDCl_3$): δ = 1.88 (s, 15H, Cp*H); 6.49 (s, 4H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 9.76 (Cp*CH_3); 90.52 (arene C–Br); 91.39 (arene C); 95.23 (Cp*). – MS (FD); *m/z* (%): 1096.1 (61.5) [(2 cations + 1 anion)$^+$], 473.0 (100) [cation$^+$]. – $C_{17}H_{21}F_3O_3SBr_2Ru$ (623.11): calcd. C 32.76, H 3.40; found C 33.16, H 3.30.

Ruthenium-Complexed Terphenyl **3**: A 25 ml Schlenk flask is charged with 126 mg (0.202 mmol) **1**, 50.2 mg (0.405 mmol) phenyl boronic acid and 137 mg (1.29 mmol) Na_2CO_3. The solids are dissolved in 2.4 ml DME and 1.6 ml water. Then 1.2 mg (0.001 mmol) $Pd(PPh_3)_4$ is added. The reaction mixture is stirred at 80 °C for three days, the reaction is quenched by adding 6 ml of cold water, where upon a white solid precipitated. The crystals are collected by filtration to yield 124 mg of **3** (99%); m.p. 284 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 3088 cm^{-1}, 2963, 2923, 2854, 1793, 1774, 1734, 1718, 1701, 1685, 1654, 1647, 1636, 1578, 1560, 1541, 1508, 1466, 1388, 1259, 1223, 1152, 1098, 1030, 773, 762, 699, 692, 638, 574, 517, 496. – ^1H NMR ($CDCl_3$): δ = 1.88 (s, 15H, Cp*H), 6.78 (s, 4H, 2′,3′,5′,6′-H); 7.62 (m, 6H, phenyl H); 7.89 (m, 4H, phenyl H). – ^{13}C NMR ($CDCl_3$): δ = 9.58 (Cp*CH_3); 84.82 (C-2′,3′,5′,6′); 95.8 (Cp*); 100.53 (C-1′,4′); 127.27, 129.48 (arene C); 130.27 (arene C); 131.89 (arene C). – MS: *m/z* (%): 1081.2 (1.1) [(2 cations + 1 anion)$^+$], 467.3 (100) [cation$^+$]. – $C_{29}H_{29}F_3O_3SRu$ (615.67): calcd. C 56.57, H 4.75; found C 56.07, H 4.82.

X-ray Crystal Structure Analysis of **3**: single crystals were obtained by letting dichloromethane slowly evaporate from a solution of **3** in this solvent at 5 °C. $C_{29}H_{29}F_3O_3SRu$ (615.67), crystal size 0.3 × 0.15 × 0.05 mm cell parameters a = 10.185(1) Å, b = 22.366(1) Å, c = 12.393(1) Å, β = 103.025(8)°, Z = 4, D_x = 1.487 g cm^{-3}, space group $P2_1/n$, CAD4 diffractometer, graphite monochromated Cu K_α radiation; Θ_{max} = 60°, 4208 reflections measured, 3297 reflections observed [$I > 3\sigma(I)$], μ = 5836 cm^{-1}, empirical absorption correction (min. transmission: 88.4 max. transmission: 97.3). The structure was solved by the heavy atom method (Patterson) and refined by full-matrix least-squares analysis with anisotropic temperature factors for Ru, C, S, O, F. The H atoms were refined in the "riding mode" with fixed isotropic temperature factors. Final R = 0.039; R_w = 0.042. Program used: MOLEN. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-405109, the names of the authors, and the journal citation.

☆ Dedicated to Professor *Günter Szeimies* with gratitude on the occasion of his 60th birthday.

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