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A Study of Palladium-Catalyzed Arylation of Bis(3-bromo-5-methyl-6*H*-cyclopenta[*b*]thien-6-yl)(dimethyl)silane

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Received August 8, 2008

DOI: 10.1134/S0012500809020037

Metallocenes of titanium subgroup due to their activation with MAO (methylalumoxane) are widely used in industry as a basis of highly active homogeneous and heterogenized catalysts of olefin polymerization [1]. Catalysts derived from so-called advanced *ansa-zir*-conocenes show high activity and stereoselectivity in propylene polymerization [2–5]. These metallocenes involve bis(2-methyl-4-arylindenyl)dimethylsilane ligands (type **A**) or similar 2,5-dimethyl-3-arylcyclopenta[*b*]thienyl fragments (type **B**) (Fig. 1).

The palladium-catalyzed arylation of bis(3-bromo-5-methyl-6H-cyclopenta[b]thien-6-yl)dimethylsilane with different arylzincates provides a basis for a new synthetic approach that facilitates the preparation of complexes of type **B** due to the introduction of aryl fragment at a later stage. This allows one to considerably decrease the number of stages in the synthesis of various aryl-substituted zirconocenes.

To obtain zirconium complexes of type \mathbf{B} by our method, it is necessary to prepare bis(3-bromo-5methyl-6*H*-cyclopenta[*b*]thien-6-yl)dimethylsilane, which is a substrate for the synthesis of corresponding aryl-containing ligands. However, the metalation of 3-bromo-5-methyl-4(5)H-cyclopenta[b]thiophene with *n*-butyllithium in an ether medium followed by the treatment of resulting lithium salt with 0.5 mol of dimethyldichlorosilane does not lead to the desired result. Along with the target 6,6'-substituted product, the reaction gives isomeric 4,6'- and 4,4'-substituted compounds containing the 3-bromo-5-methylcyclopenta[b]thien-4-yl fragment (Scheme 1). The content of the 6,6'-isomer (the first compound) in the resulting mixture was about 60%. However, we failed to isolate the target product in the pure state. All three compounds obtained have close solubility, which hampers the isolation of the 6,6'-isomer by crystallization. The use of other methods for purification is either impossible (e.g., distillation) or rather difficult (e.g., chromatography). The observed regioselectivity of the reaction is likely to be explained by the fact that the bromine atom in 3-bromo-5-methylcyclopenta[b]thiophene is rather distant from the cyclopentadienyl fragment and, hence, cannot provide the sufficient steric shielding of the nearest carbon atom in the cyclopentadienyl ring. It is known that the organosilyl substituents in cyclopentadiene and its derivatives can participate in the 1,3-sigmatropic rearrangement even at ambient temperature [6]. In the reaction under consideration, the thermodynamic stability of isomeric silyl-substituted products seems to be close; therefore, the total stereocontrol in the synthesis of the corresponding bridge ligand is impossible.



Fig. 1. Advanced zirconocenes.

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However, the problem was solved unexpectedly owing to subsequent cross-coupling reaction. The mixture

of products **2** was found to form a sole isomer containing the aryl group in the desired position (Scheme 2).





The Negishi reaction of organozinc compounds was used as the main procedure for the cross-coupling reaction [7]. The initial arylzinc chlorides were obtained in situ by the reaction of zinc chloride with the corresponding Grignard reagent in THF. The cross-coupling reaction was conducted for several hours at 70°C. A catalyst used was $Pd(t-Bu_3P)_2$, whose high activity was shown by us in similar studies with participation of bis(4-bromo-2-methyl-1*H*inden-1-yl)dimethylsilane.

The result is explained by the ease of 1,3-sigmatropic rearrangement for the organosilicon derivatives of cyclopentadienes and their analogues [6] and by the lower thermodynamic stability of isomers where the bulky aryl fragment is located in close proximity to the Si Me_2 bridge. As a result, the products of arylation of isomeric bridging ligands containing 3-aryl-5-methylcyclopenta[b]thienyl fragments with the silyl substituent in the 4-position undergo rearrangement into less sterically hindered products containing the silyl substituent in the 6-position. Thus, the observed isomerization of the products of the cross-coupling reaction allows us to avoid the laborious procedure of separation of isomeric bridging ligands and allows the simple preparation of a number of interesting compounds for the further synthesis of *ansa*-metallocenes.

The obtained ligands 3a and 3b were involved into preparation of the corresponding zirconocenes. The synthesis was carried out according to the procedure in [8] by the metalation of the initial ligand with *n*-butyllithium in ether followed by the reaction of the dilithium salt of the ligand with zirconium tetrachloride tetrahydrofuranate (Scheme 3).





Thus, in this study we have developed a new approach to the synthesis of aryl-substituted (cyclopenta[b]thienyl)dimethylsilanes via the palladium-catalyzed Negishi arylation of corresponding bromo-substituted substrates. The initial bromo-substituted bridging ligands with cyclopenta[b]thienyl fragments are the mixtures of regioisomers that differ in the position of the bridging fragment toward the halogen atoms; none-theless, the resulting products of the Negishi reaction undergo rearrangement to give a sole isomer necessary for the synthesis of *ansa*-metallocenes.

EXPERIMENTAL

All experiments with moisture- and oxygen-sensitive compounds were carried out in an argon atmosphere using the standard Schlenk technique or in a box with a controlled nitrogen atmosphere. Analyzes were performed on a Waters Delta 600 chromatograph. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 400 DPX spectrometer operating at 400 and 100 MHz, respectively. Elemental analysis was accomplished using a Heraeus CHN-O-Rapid analyzer. 5-Methyl-4,5-dihydro-6*H*-cyclopenta[*b*]thiophen-6one was obtained from thiophene and metacrylic acid as described in [9]. 3-Bromo-5-methyl-4(5)H-cyclopenta[b]thiophene was prepared by the bromination of 5-methyl-4,5-dihydro-6H-cyclopenta[b]thiophen-6one followed by reduction and dehydration by the procedure in [9].

Bis(3-bromo-5-methyl-6*H*-cyclopenta[*b*]thien-6yl)(dimethyl)silanes (2). A 1.6 M solution of *Me*Li (16.0 mL, 25.6 mmol) in diethyl ether was added to a solution of 5.50 g (25.6 mmol) of 3-bromo-5-methylcyclopenta[*b*]thiophene in 250 mL of ether at -60° C. The mixture was stirred for 1 h at ambient temperature and cooled to 0°C, and 1.55 mL (1.65 g, 12.8 mmol) of *Me*₂SiCl₂ was added. The reaction mixture was stirred for 12 h at ambient temperature, and 50 mL of water was added. The organic layer was separated and dried with K₂CO₃, and the solvent was removed on a rotary evaporator. The residue was purified by flash chromatography on silica gel (40–63 µm, column 40 mm in

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diameter and 500 mm long, hexane as eluent) to give 2.61 g (42%) of a mixture of 6,6'-isomer (about 60%) with 4,4'- and 4,6'-isomers (about 40%).

Procedure for the Negishi reaction. A 1.0 M solution of the corresponding Grignard reagent (26.0 mL, 26.0 mmol) in THF was added to 58.0 mL of a 0.50 M solution of ZnCl_2 (29.0 mmol) in THF at ambient temperature. The reaction mixture was stirred for 1 h, and then 10.0 mmol of a mixture of compound 2 and 20.0 mL of a 0.02 M solution of Pd(*t*-Bu₃P)₂ (0.40 mmol) in THF was added. The mixture was stirred at 70°C for 5 h, cooled, and passed through a silica gel bed (30 mm in diameter, 50 mm in height, THF as eluent). The solvent was removed on a rotary evaporator. The product (**3a**, **3b**, **3c**) was isolated by flash chromatography on silica gel (40–63 µm, a column 30 mm in diameter and 100 mm long, hexane as eluent).

General procedure for the preparation of ansazirconocenes. A 2.5 M solution of *n*-BuLi (7.92 mL, 20.0 mmol) in hexane was added to a solution of 10.0 mmol of ligand **3a** or **3c** in 220 mL of diethyl ether at ambient temperature. The reaction mixture was stirred for 24 h and then cooled to -78°C, and 10.0 mmol of ZrCl₄(THF)₂ was added. The mixture was stirred for 24 h at ambient temperature, and the solvent was removed to drvness. Toluene (220 mL) was added to the residue, the mixture was stirred for 8 h at 90°C, and the hot solution was filtered through a G4 porosity sintered glass filter. The residue was additionally washed with hot toluene $(3 \times 100 \text{ mL})$. The combined extracts were evaporated to dryness. Product 4a or **4b** was isolated by the crystallization of the residue from dichloromethane.

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