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### Streszczenie w j. angielskim pracy doktorskiej

pt. „Zastosowanie hydrometalowania wiązań wielokrotnych węgiel-węgiel w syntezie boro- i krzemooorganicznych bloków budulcowych dla chemii organicznej i materiałowej”

„The application of hydrometallation of carbon-carbon multiple bonds in the synthesis of organoboron and organosilicon building blocks for organic and material chemistry”

Hydroboration and hydrosilylation are among the most commonly used hydrometalation processes. These are addition reactions of hydroboranes and hydrosilanes to the carbon-carbon multiple bonds, respectively. They are simple, one-step procedures for introducing boryl and silyl groups into the structure of compounds and are the most often used in the synthesis of this type of products. Hydrosilylation and hydroboration are usually carried out in the presence of transition metal complexes as catalysts, allowing for effective control of the regio-, stereo-, and chemoselectivity of the process, leading to final products with a strictly defined topology. Moreover, they are characterized by a 100% atom economy, which allows for the efficient, waste-free synthesis of fine chemicals, drugs, silicones, silane coupling agents, rubbers, and many others. The presence of organoboron and organosilicon groups susceptible to functionalization through coupling and demetalation processes makes these compounds often used as building blocks in the synthesis of natural products, pharmaceuticals, or dyes. On the other hand, introducing these groups into the structure of the product significantly affects the change of their physical and chemical properties, allowing for their application in material chemistry. One such example is silane coupling agents, the global market of which is currently over USD 1.2 billion, and it is estimated that it will have increased to USD 1.6 billion by 2026. They are used in the synthesis of inorganic-organic hybrid materials, improving the compatibility between components, resulting in improved performance of final products, i.e. hardness, mechanical and thermal resistance, and adhesion.

One of the main areas of application of coupling agents is the rubber industry, in particular, the production of car tires. The most critical challenge facing the modern tire industry is to reduce the energy consumption of the transport sector, which is responsible for over 20% of the total energy consumption in the world, with 20-30% of fuel consumption related to the rolling resistance of tires. Moreover, 18% of global carbon dioxide emission comes from road traffic, of which 24% are due to the phenomena that tires undergo while driving. To meet these problems, in the last decade of the 20<sup>th</sup> century, the first energy-efficient tire was produced using elastomeric composites reinforced with silica in the presence of polysulfide silane coupling agents. These tires were characterized by reduced rolling resistance and increased wet grip compared to tires previously manufactured using only carbon black as a filler. The design and synthesis of new silane coupling agents with unique structures and properties are essential in increasing driving safety and counteracting negative climate change. This perfectly fits the sustainable development policy defined by the United Nations in the 2030 Agenda.

Considering the extraordinary usefulness of hydrometallation processes in the synthesis of new building blocks and materials, the aim of this doctoral dissertation entitled "*The application of hydrometallation of carbon-carbon multiple bonds in the synthesis of organoboron and organosilicon building blocks for organic and material chemistry*" is the development of efficient and selective methods for the synthesis of organoboron and organosilicon compounds, so far undescribed in the literature, which, on the one hand, can be used as building blocks in organic synthesis, and on the other as components in the production of modern materials. The literature review clearly indicated that the hydroboration of conjugated 1,3-dienes is sparsely described in scientific publications. Therefore, this topic has become the subject of research in this dissertation. The possibility of creating several different products and isomers in the hydroboration of 1,3-dienes is a challenge because of process selectivity, and seeking effective methods of their functionalization is extremely important from the perspective of the synthesis of conjugated compounds.

Another task undertaken in this work was the application of hydrosilylation of olefins and alkynes with triethoxysilane and 2,4,6,8-tetramethylcyclotetrasiloxane in the production of new silane coupling agents and their further use in the production of "green tires". This part of the thesis was carried out in cooperation with Synthos S.A., a leader in the production of styrene-butadiene rubbers.

Therefore, the doctoral thesis includes a series of three publications containing research on the modification of structurally complex reagents by hydroboration and hydrosilylation reactions (**P1-P3**). These articles describe the synthesis, characterization, and application studies of monoboryl-substituted enynes (**P1**), as well as bifunctional silanes having an aromatic core of naturally occurring eugenol (**P2**), and the synthesis of branched cyclosiloxanes decorated with four groups of two types (**P3**).

Commercially available transition metal complexes were used in the developed protocols, i.e.,  $[\text{Ru}(\text{CO})\text{Cl}(\text{H})(\text{PPh}_3)_3]$ ,  $[\text{Ir}(\text{cod})\text{Cl}]_2$ , and Karstedt's catalyst  $[\text{Pt}_2(\text{dvs})_3]$ . The selection of the appropriate catalyst (type and concentration) and the optimization of the reaction conditions (reactant ratio, reaction temperature, or type of solvent used) allowed to obtain the desired products with high yield and regio- and stereoselectivity (or chemoselectivity), using mild reaction conditions, avoiding the generation of by-products. Such approach fits into the realization of processes under the principles of Green Chemistry.

Within this research, 7 boryl-substituted enynes and 7 corresponding trifluoroborate salts, 24 bifunctional, aromatic organosilanes obtained by modification of eugenol and 13 derivatives of 2,4,6,8-tetramethylcyclotetrasiloxane, having in their structure four chemical groups of two types in a strictly defined ratio were synthesized. The obtained compounds have a unique structure, and most of them have not been described in the literature so far.

All synthesized products were fully characterized by spectroscopic methods ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{11}\text{B}$ ,  $^{29}\text{Si}$  NMR, 1D NOESY NMR) and spectrometric methods (MALDI MS, ESI MS, EI MS), as well as using elemental analysis. In addition, bifunctional organosilanes with alkoxy silyl groups were applied to prepare silica-reinforced styrene-butadiene composites in cooperation with Synthos company. Improvements in rolling resistance and traction on wet and icy surfaces were observed, which positively affect driving safety, lower fuel consumption, and reduce the amount of generated carbon dioxide. The obtained results indicate the application potential of the synthesized compounds in the production of new elastomeric composites for tire treads with improved performance.