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Kompleksy tytanu i cyrkonu z ligandami N-, O-donorowymi w polimeryzacji i syntezie enancjoselektywnej=Titanium and zirconium complexes with n-, o-donor ligands for polymerization and enantioselective.

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Streszczenie

Kompleksy metali przejúciowych IV grupy z ligandami aryloksanowymi1.1. Kompleksy tytanu i cyrkonu z ligandami aryloksanowymi1.1.1. Kompleksy tytanu i cyrkonu z ligandami monoaryloksanowymi1.1.2. Kompleksy tytanu i cyrkonu z ligandami bisaryloksanowymi1.1.3. Kompleksy tytanu i cyrkonu z ligandami
trisaryloksanowymi1.2. Kompleksy tytanu i cyrkonu z ligandami imino-aryloksanowymi1.2.1. Budowa i synteza ligandÛw1.2.2. Budowa i synteza kompleksÛw1.3. Kompleksy tytanu i cyrkonu z ligandami amino-aryloksanowymi1.3.1. Budowa i synteza ligandÛw1.3.2. Budowa i synteza kompleksÛw2. Zastosowanie kompleksów metali przejúciowych IV grupy w katalizie2.1. Budowa i aktywnoúÊ katalityczna aryloksanowych kompleksów tytanu i cyrkonuw polimeryzacji cyklicznych estrÛw2.2. Budowa i aktywnoúÊ katalityczna aryloksanowych kompleksÛw tytanu i cyrkonuw polimeryzacji a-olefin2.3. Kataliza enancjoselektywna2.3.1. Kompleksy tytanu i cyrkonu jako katalizatory reakcji addycji acetylenu doaldehydu2.3.2. Kompleksy tytanu i cyrkonu jako katalizatory reakcji addycji trimetylosililo-cyjanku do benzaldehydu2.3.3. Kompleksy tytanu i cyrkonu jako katalizatory reakcji aldolowych.

Witnessed within the last decades rapid development of the chemistry of Group 4 metals can be ascribed to the interesting structural properties of such complexes, as well as to wide range of their industrial applications. Species of titanium and zirconium bonded to aryloxo ligands are very good fodder for asymmetric organic syntheses, are very often used as base compounds for material engineering and catalysts or initiators for different kind of polymerization processes, and also for production of biodegradable materials. A carefully chosen ligand plays a crucial role in construction of potential candidates for these applications. Aryloxides form a big family of mono-, bis- and poliaryloxo ligands. They are very versatile since their structure and

electronic properties are easily modified by changing of ring substitution patterns [10, 11], introducing of O, S, NR, Se, Te heterogroups [21] between aromatic rings [12-14], changing their numbers [15, 16] or even linking them by carbon chains [17, 18]. All those modifications can influence the structure and catalytic activity of formed complexes. Apart from aryloxides, also amino- and iminoaryloxides form the second group of ligands successfully utilized in chemistry of Group 4 metals. Chemical properties of these ligands can be easily modified through changing aromatic rings by using substituents influencing electronic properties and steric demands. For example, nitrogen atom changed by introduction of a group containing additional centre of coordination results in obtaining tridendate ligand [43]. Mannich condensation is the main synthetic method for obtaining these compounds [47]. Usage of primary, secondary or tertiary amine, as well as a change in reaction stechiometry or even a condition can lead to amine-aryloxide, amine-bisaryloxide or benzoxazine. Syntheses of transition metal compounds with aryloxide or amine/iminearyloxide species are generated by direct ligand reaction with a metal precursors MRn, M(OR)n, M(NR2)n, MCln (R = alkyl). Monodendate aryloxo ligands have a tendency to form ?-bridges between metal centres, which result in formation of oligomeric compound [M(OAr)n]m. Reactions of bisaryloxo ligands H2(LEtBu,Me) (E = -, CH2, C2H4) with chosen titanium and zirconium precursors produce heteroleptic, monomeric and tetrahedral complexes [12, 19, 20]. Change of a bridging group between phenyl rings to C2H4 increases the size of chelating ring in formed complexes [MX2(LC2H4tBu,Me)] [20, 35, 36] and at the same time decreases the inversion barrier which is the reason for relatively easy conformation changes in solutions. Imine-aryloxide complexes of Group 4 metals have been known since 1960 [44], but mainly in last decade we can witness the rapid development of this group. Here, one of the most interesting species are complexes with tetradendate amino-bisaryloxo ligands. These compound can adapt a different symmetry which depends on a ligand structure, with additional electron pair donor D [10]. First literature reports on the use of titanium complexes in polymerization of cyclic esters are from 1958 [61]. Mono-, and bisaryloxide complexes were reported to act as initiators for that reaction but the highest activity was obtained when heteroleptic titanium compounds supported by tridendate ligand (H2LN-R'tBu) [48] were used. Catalytic activity in lactide polymerization on titanium and zirconium complexes strongly depends on metal and aromatic rings substituents . Transition metal complexes of Group 4 metals stabilized by aryloxo and imine/aminearyloxo ligands play a very important role among relatively new non-metalocene catalysts for olefin polymerization. Monoaryloxide complexes are not effective in that process [66], titanium and zirconium species with bisaryloxo ligands, in which aromatic rings are linked by CH2 are less effective in ethene [68, 69] polymerization when compared to cyclopentadienyls [70]. Zirconium and hafnium amine-bisaryloxides are highly effective in 1-hexene polymerization and structure of a ligand plays here a key role [15]. Additional donor of electron density is also an important factor influencing molecular mass and polymer tacticity. Imine-aryloxide species with bulky groups in ortho- or NO2, OMe in para- positions are highly effective in polyethylene production. In asymmetric syntheses titanium and zirconium species are used for different processes, for example enantioselective oxidation, reduction, nucleophilic addition, cycloaddition and many others [81-84].

Słowa kluczowe

titanium, zirconium, aryloxide complexes, catalysts/initiators, lactide polymerization, enantioselective sythesis

tytan, cyrkon, kompleksy aryloksanowe, katalizatory/inicjatory, polimeryzacja laktydów, synteza enancjoselektywna

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